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Formation of transition metal silicides by solid–gas reactions: thermodynamic and kinetic considerations

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Abstract

Alternative synthesis routes to nickel silicides are discussed. Results of the reactions of Ni with a $SiCl_4/H_2$ gas mixture (1), of NiSi with $NiCl_2$ (2) as well as of Si with nickel halides (3) are presented. Kinetics of the reactions (1) and (2) were studied in detail by in situ electrical resistance measurements and isothermal X-ray powder diffraction, respectively. Kinetic evaluation of the electrical resistance measurement data points to island and layered silicide growth in process (1). XRD data analysis leads to the conclusion that process (2) proceeds via transient metastable nickel silicide phases, which are interrelated with the thermodynamically stable silicide phases Ni_2Si, Ni_3Si_2 and NiSi. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicide; In situ electrical resistance measurements; Kinetics; Solid–gas reaction
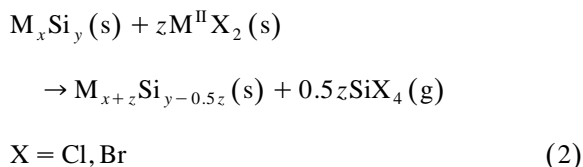
1. Introduction

Transition metal silicides are commonly prepared by melting the elements in a temperature range from 1400°C to 2500°C (Eq. (1)). In spite of high temperatures, products of well-defined stoichiometries are not always obtained. Frequently, annealing for some days or even weeks is required.

The present work is focused on such reactions, which allow a fast and selective formation of transition metal silicides or conversion of silicide phases into other ones.

(1) Reaction of a transition metal M with $SiCl_4/H_2$ gas mixture.

$$x M(s) + y SiCl_4(g) + 2 y H_2(g)$$
$$\rightarrow M_x Si_y(s) + 4 y HCl(g) \tag{1}$$
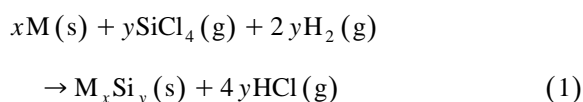
(2) Conversion of a metal silicide via reaction with metal chloride yielding a metal-rich silicide phase.

$$M_x Si_y(s) + z M^{II} X_2(s)$$
$$\rightarrow M_{x+z} Si_{y-0.5z}(s) + 0.5 z SiX_4(g)$$

$$X = Cl, Br \tag{2}$$

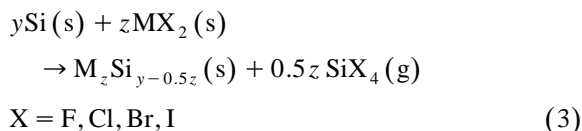These results are compared with those obtained from reaction of silicon with transition metal chlo-

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rides to provide information about rate and selectivity of these processes.

$$y\text{Si}(s) + z\text{MX}_2(s)$$
$$\rightarrow \text{M}_z\text{Si}_{y-0.5z}(s) + 0.5z\,\text{SiX}_4(g)$$
$$\text{X} = \text{F, Cl, Br, I} \tag{3}$$

The present work is focused on the nickel–silicon system.

2. Experimental

The apparatus consists of a quartz glass reactor with a frit inside, an oven with a thermocouple (NiCr–Ni) in the height of the reaction zone, a mass-flow-controller (Bronkhorst) for dosing the hydrogen (Air liquide, 99.999%), a liquid-flow-meter (Bronkhorst) for dosing the liquid SiCl_4 (Wacker Chemie, semiconductor grade), a controlled evaporator and mixer unit (Bronkhorst), and a gas chromatograph (GCHF 18.3, Chromatron) for quantitative analysis of the product gases (a detailed description is given in Ref. [1]). In the experiments described below, a SiCl_4 to H_2 ratio of 1:6 was chosen. All syntheses were carried out between 600°C and 1000°C.

The in situ electrical resistance measurements of the silicidation were performed using a nickel wire (diameter 0.20 mm), wound to a coil. Resistance data was taken by the four-probe method. The coil was placed inside the quartz tube, exactly in the reaction zone level. Lead-in wires were protected against the SiCl_4/H_2 atmosphere by corundum capillaries. The nickel wire was heated up in H_2 atmosphere to the desired temperature and then SiCl_4 was added.

Solid samples were characterized by X-ray powder diffraction (Siemens D-5000) as well as by SEM-EDX (Jeol JSM 6400, EDX: Noran). Thermal investigations were performed in a TG-DSC 111 (Setaram).

3. Silicide preparation by solid–gas reaction

Almost all transition metals have been studied in the procedure based on reaction (1) between 600°C and 1000°C. Obviously, the metal reactivity in this process is gradually depending on the valence electron state of the metals. Fe, Co, Ni, V, and Mo react effectively and most of the known silicide phases are formed. These 3d-metals and Mo (4d) have a lower metal-to-metal atom binding energy in comparison with the 5d-metals. The upper temperature limit of the apparatus of 1000°C has restricted our efforts to convert also the 4d- and 5d-metals. Under these conditions, finely dispersed 4d- and 5d-metals (except Mo, which gives well-defined silicides) gave only a thin layer of silicon-rich alloys on the bulk metal. Nevertheless, it seems clearly that silicides of all these metals should be accessible if we are able to set up a proper temperature level. Some metals, i.e. Cr, Ti, Zr, and Mn, form stable metal chlorides in the SiCl_4/H_2 atmosphere. Noble elements of the 8, 9, and 10 group as well as copper are easily converted into silicides. Au and Ag were not yet studied.

Reaction (1) is fully reversible. For a certain temperature, the metal picks up silicon from the gas phase until the thermodynamically stable silicide phase, corresponding to the set temperature level, is accomplished. With increasing temperature, step by step the next silicide phases, having higher silicon contents, are formed (Fig. 1a). Lowering the temperature results in depletion of the present silicide phase by its reaction with the always-present hydrogen chloride. A silicidation, starting from a pure metal or from any already formed silicide phase, is accompanied by the production of trichlorosilane HSiCl_3. Its content in the exhaust gas continuously increases with the progressing reaction. A constant remaining HSiCl_3 content indicates the entire formation of the new silicide phase. Lowering the silicon content of the solid phase by decreasing the process temperature gives rise to a temporarily higher trichlorosilane production according to Eq. (4).

$$\text{M}_x\text{Si}_y(s) + 3\text{HCl}(g)$$
$$\rightarrow \text{HSiCl}_3(g) + \text{M}_x\text{Si}_{y-1}(s) + \text{H}_2(g) \tag{4}$$
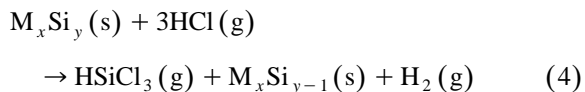
Silicide formation according Eq. (1) is fully characterized by equilibrium calculations. Based on optimized thermodynamic data of the Ni–Si system, the temperature depending silicide phase formation sequence was calculated (Fig. 1) [2]. In order to prove the validity of the optimized data, nickel silicide
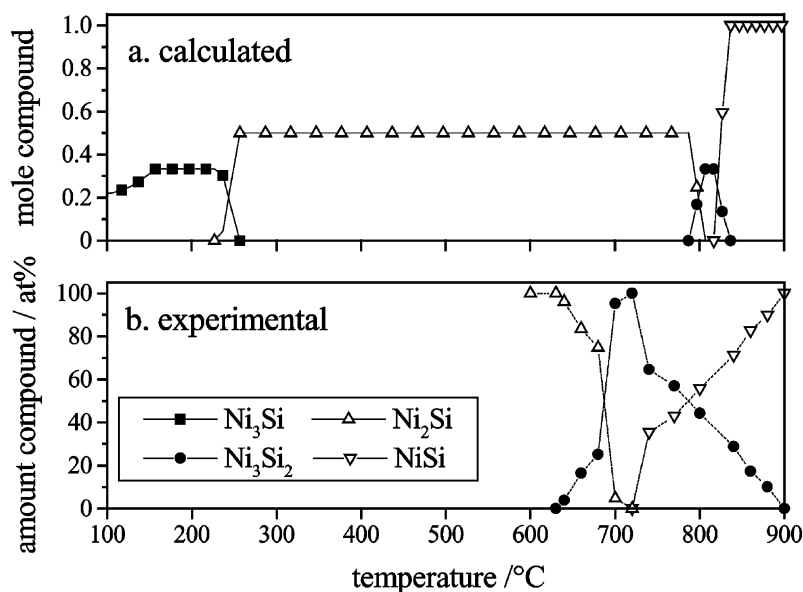
Fig. 1. Formation of nickel silicides according to Eq. (4) as function of temperature, calculated (a) and experimental (b) determined nickel silicide formation sequence.

samples were synthesized at temperatures between 600°C and 900°C in steps of 20 K. Each obtained equilibrium phase composition was analyzed by quantitative X-ray powder diffraction (Fig. 1). Defined silicide mixtures were used for calibration, the error of these measurements is about 2%.

Uncertainties in the determination of the silicide phase fractions arise at temperatures above 850°C. Ni_3Si_2 decomposes in a peritectic reaction at 845°C, but Ni_3Si_2 is still present above 845°C. The solid products, after removing from the reactor, were compact pieces. Due to the rapid diminishing of the surface area, the rate of equilibration is dramatically decreased and, thus Ni_3Si_2 is still present.

Calculated and experimentally determined silicide phase sequences are in remarkable good accordance. The differences of the formation temperatures between the calculated and the experimentally obtained phase composition are relatively small. The experimentally determined formation temperature of e.g. Ni_3Si_2 agrees with the calculated ones, if the formation enthalpy of Ni_3Si_2 is corrected from -231.05 kJ mol^{-1} [2] to -237.70 kJ mol^{-1}, which represents a deviation less than 3%. Furthermore, it should be noted that a calculation of the sequence with earlier data [3] gave absolutely no correspondence with the experimental results (e.g. no appearance of Ni_3Si_2) [2].

The initial period of silicide formation process is of special interest. Therefore, the silicidation process was followed by in situ electrical resistance measurements of nickel wires at temperatures between 650°C and 800°C. The measurements are based on significant differences in the electrical resistivity of the involved adjacent compounds Ni/Ni_2Si, Ni_2Si/Ni_3Si_2, and $Ni_3Si_2/NiSi$ (Table 1) as well as on the assumption that these differences remain almost unchanged at high temperatures.

Fig. 2 shows the resistance curve and the corresponding trichlorosilane content of the exhaust gas during the silicidation of a nickel wire at 800°C. The equilibrium composition of the solid phase amounts at this temperature to 44 at.% Ni_3Si_2 and 56 at.% NiSi. First, an induction period of a slight linear resistance increase and a minimal $HSiCl_3$ formation

Table 1
Resistivity of nickel silicides at 20°C

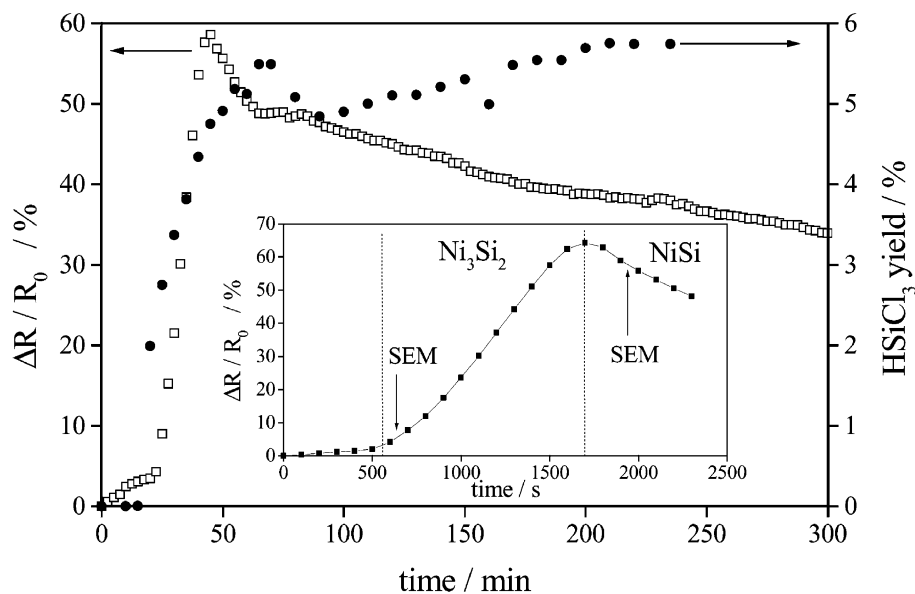|	NiSi	Ni_3Si_2	Ni_2Si	Ni
ρ (293 K) [$\mu\Omega$ cm]	20.2 [4]	79 ± 7 [4]	20 [4]	6.9 [5]
	10.5 [5]		24 [5]	

Fig. 2. Relative resistance change and trichlorosilane yield of the silicidation of a nickel wire at 800°C. Inset: The initial period of silicidation: ranges of Ni_3Si_2 and NiSi formation are indicated, interruption of identical experiments for SEM-EDX investigation of the wire. Arrow at about 650 s corresponds to the micrograph in Fig. 3 (left), arrow at about 1950 s corresponds to the micrograph in Fig. 3 (right).

is observed. The length of this induction period is reduced with increasing temperature. It follows a period, which is characterized by both a strong increase in resistance and $HSiCl_3$ content, arising from the formation of Ni_3Si_2. After a maximum resistance value is reached, the formation of NiSi occurs and the resistance decreases. A drop in a resistance value is not caused only due to a lower electrical resistance. All results are superimposed by enlargement of the wire cross-section during the metal silicidation. Finally, after a reaction time of about 5 h, both a nearly constant resistance and $HSiCl_3$ yield indicate the equilibration of the reaction.

In identical measurements, the experiments were interrupted after the process of a certain time run. The cross-section of the wire was analyzed by SEM-EDX. Two points of such analysis were marked in the inset of Fig. 2, which demonstrates the initial silicide formation period in more detail. Fig. 3 (left picture) shows the SEM micrograph after a silicide formation period of 650 s. The wire exhibits fractures and cracks as a result of the silicidation. Within almost compact matter, islands of different stages of silicidation can be recognized. The phase composi-

tion at points A and B corresponds approximately to Ni_3Si_2, whereas nickel at points C and D was found with about 1 at.% Si and chlorine. (The chlorine content of the original sample may be higher, but it could decrease when the samples are polished. The chlorine is assumed to be located below the surface of the sample, where it is protected by the silicide and detected only by the penetration depth of the electron beam.) The XRD analysis reveals the presence of Ni_3Si_2 and Ni. The micrograph in Fig. 3 (right picture) was recorded from a sample after a silicide formation period of 2000 s. It shows a layer of NiSi grown on a core of Ni_3Si_2, which is consistent with the XRD analysis. A depth profile of the sample (Fig. 4) reveals a thickness of the NiSi layer of about 35 μm. The transition range from NiSi to Ni_3Si_2 is yet unclear. No mixing phase of both compounds is known. It is assumed that the NiSi layer has no uniform thickness, and thus the composition in the phase boundary region is averaged out by the penetration depth of the electron beam of the EDX.

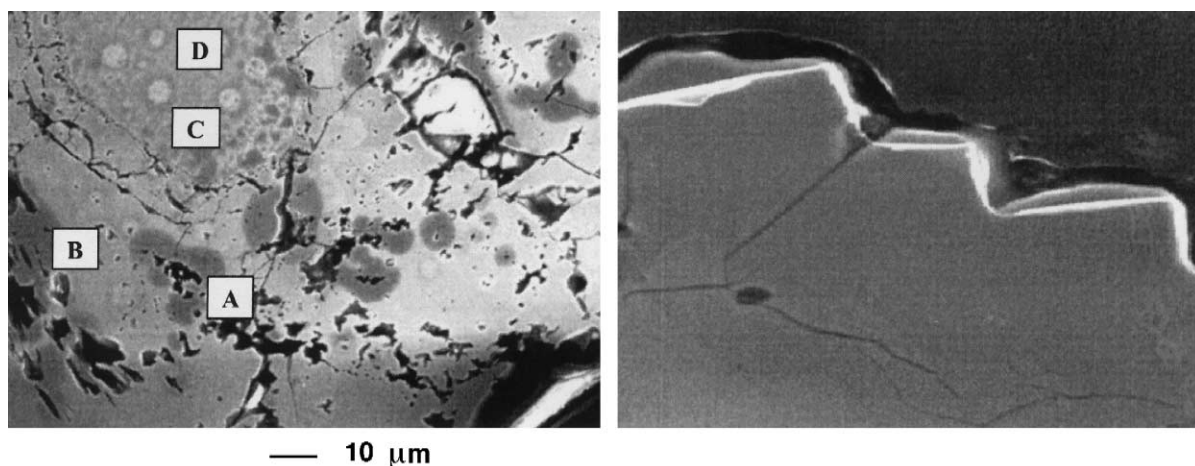Similar results were obtained at a temperature of 680°C. In this case, a mixture of Ni_3Si_2 and Ni_2Si is

Fig. 3. SEM micrograph of a nickel wire. Left: after 650 s silicidation at 800°C. (A) 62.7 at.% Ni, 37.0 at.% Si, 0.3 at.% Cl; (B) 58.0 at.% Ni, 42.0 at.% Si; (C) 98.7 at.% Ni, 0.9 at.% Si, 0.4 at.% Cl; (D) 99.3 at.% Ni, 0.7 at.% Si. Right: after 1950 s silicidation at 800°C.

formed. At 720°C only Ni_3Si_2 is produced. Here, both resistance and $HSiCl_3$ content remain almost constant after reaching their maximum values.

The formation of nickel silicides via reaction (1) can be described by three essential steps.

1. Formation of an external silicon-rich layer in an induction period, which corresponds to a negligible formation of trichlorosilane. The time-dependence of the resistance shows a definite layered growth.
2. Growth of the metal-rich silicide phase. The linear resistance gradient indicates an island formation [6,7]. The trichlorosilane content increases rapidly.
3. Layered growth of the next silicon-rich silicide compound on the underlying metal-rich silicide compound. Changes in the resistance and in the $HSiCl_3$ content are small.
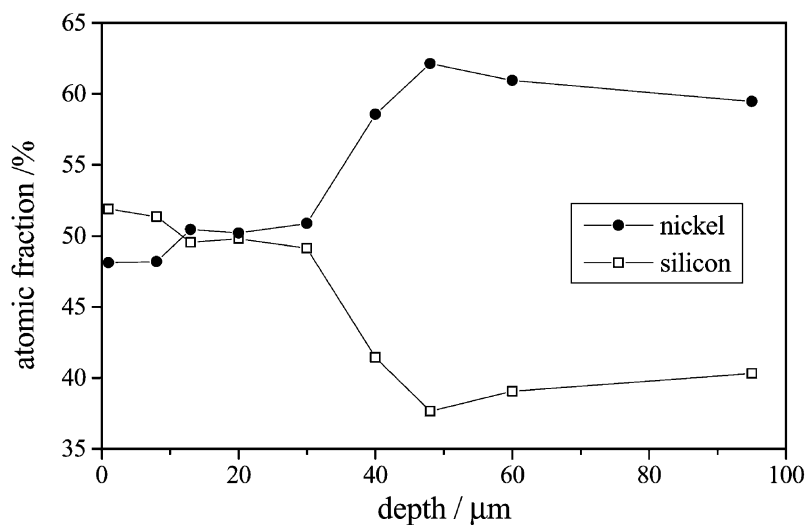

Fig. 4. Depth profile of the surface region of a nickel wire after silicidation at 800°C. The sample was taken after reaching the maximum of the resistance curve.

The strongly linear increase of the electrical resistance vs. time (step 2) was used for the evaluation of kinetic data. It is assumed that the total electrical resistance is the sum of the resistance of the metal and of the silicide (Eq. (5)). For the sake of simplicity, the volume change during silicidation process was neglected.

$$R = ((1 - w_2)\rho_1 + w_2\rho_2)/\pi r^2$$
$$= (\rho_1 + w_2(\rho_2 - \rho_1))/\pi r^2 \qquad (5)$$

R—resistance of the wire; ρ_1, ρ_2—specific resistance of nickel and silicide, respectively; w_1, w_2—mass fractions of nickel and silicide, respectively; l—length of the wire; r—radius of the wire. R_0 represents the electrical resistance of the wire at the time $t = 0$ (Eq. (6)).

$$1/\pi r^2 = R_0/\rho_1 \qquad (6)$$

From Eqs. (5) and (6), expression (7) results.

$$(R - R_0)/R_0 = (\rho_2 - \rho_1)w_2/\rho_1 \qquad (7)$$

Furthermore, the molar fraction of the silicide is assumed to increase linearly with time according to a rate law of zero order $w_2 = k(T)t$. In the resulting Eq. (8), the term $k(T)$ is substituted by an expression of the linear slop of the resistance vs. time curve $s(T)$.

$$(R - R_0)/R_0 = (\rho_2 - \rho_1)/\rho_1 k(T)t = s(T)t \quad (8)$$

Fitting the experimental data between 700°C and 800°C (Ni_2Si is formed first as a metal-rich compound below 700°C) with Eq. (8) results in Eq. (9).

$$\ln k(T) = -16325/T + 12.28 \qquad (9)$$

From this relation, an activation energy of 136 ± 9 kJ mol^{-1} is derived. To our knowledge, an activation energy of the formation of Ni_3Si_2 has not been published yet. The order of magnitude corresponds to a value for Ni_2Si of 145 kJ mol^{-1} determined in thin layer diffusion experiments [8,9].

4. Silicide formation by the reaction of a transition metal silicide or silicon with transition metal halogenides

Silicon-rich transition metal silicide phases can easily be converted into metal-rich phases by reaction with their corresponding metal chloride, according to Eq. (2). If the process is carried out in sealed quartz ampoules at 700°C (for Fe, Co, Ni) for 2 weeks, each silicide phase having a metal content higher than the initial used silicide can be obtained, exactly according to the stoichiometry of the educt mixture and to equilibrium calculations. As a representative, the reaction of NiSi and NiCl$_2$ in a molar ratio of 7:2 under formation of Ni$_3$Si$_2$ is described in more detail (Eq. (10)).

$$7NiSi(s) + 2NiCl_2(s) \rightarrow 3Ni_3Si_2(s) + SiCl_4(g)$$
$$(10)$$
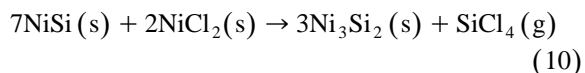
Reaction (10) was identified as a solid–gas reaction. Heating up NiSi and NiCl$_2$ in an open system (TG-DSC), the reaction occurs at 640°C (Fig. 5a). The obtained solid product is a crude mixture of different silicides and nickel metal. In case of heating up NiSi and NiCl$_2$ in a closed system (sealed crucible, Fig. 5b), the reaction starts at 350°C and the solid products are Ni$_2$Si and nickel metal. For reaction (10), the process conditions determine significantly the mechanism of the proceeding reaction. In an open system, the reaction takes place between NiSi and gaseous NiCl$_2$. The NiCl$_2$ partial pressure [10] at 640°C is about a few millibar, which is high enough for a chemical reaction. This very fast reaction does not allow the formation of a defined solid product.

In Fig. 5, for both systems a small exothermic process occurs at 350°C. For the closed system, the conclusion is drawn that reactive gaseous products evolve at this point. If they remain in the system, their presence opens another reaction path and the mechanism is changed. It had been shown for the closed system [11] that traces of moisture are adherent to NiCl$_2$ (less than 1 wt.%). At about 340°C, hydrogen chloride HCl is liberated as a result of the hydrolysis of NiCl$_2$ (small peak in Fig. 5b). HCl reacts with NiSi mainly forming SiCl$_4$, H$_2$ and HSiCl$_3$. SiCl$_4$ is inactive in that process, but H$_2$ and HSiCl$_3$ react with NiCl$_2$ under formation of nickel metal and HCl. As long as NiCl$_2$ is present in the closed system, HCl is continuously regenerated and nickel is formed. The reaction of NiSi with HCl and the subsequent reaction of the produced silicide phase with nickel are the essential steps of the low temper-
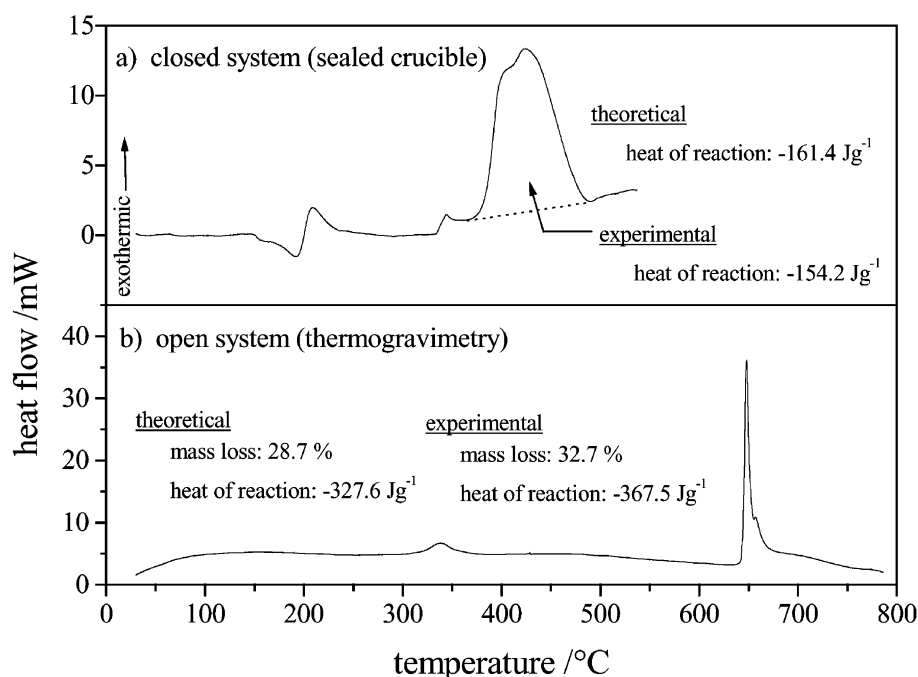
Fig. 5. Heat flow curves of reaction (10) in an open system (a) and in a closed system (b).

ature mechanism, which is not obvious in Eq. (9). Therefore, the initial period is described in more detail.

For short process periods in sealed quartz ampoules, it depends mainly on the reaction temperature, but also on the particle size of NiSi, which solid products are formed in reaction (10). Between 400°C and 450°C and tempering periods up to 20 min the solid products are Ni_2Si and nickel metal. Ni exclusively arises from $NiCl_2$, but not from a decomposition of NiSi [11]. With increasing temperature, the elemental nickel becomes more mobile and diffuses into Ni_2Si. Nickel metal was no longer present in samples prepared up to 15 min at 550°C. In spite of a molar composition of Ni:Si of about 3:2 (determined by EDX), Ni_3Si_2 was not yet found by XRD. The absence of Ni_3Si_2 at temperatures below 600°C is attributed to a hindered nucleation [12]. In our experiments, Ni_3Si_2 (and Ni_2Si) was found above 550°C.

It can be concluded that reaction (10) proceeds in two steps:

1. Formation of a metastable kinetically determined silicide phase (by the reaction of NiSi

and HCl) and nickel metal (from the reduction of $NiCl_2$ by H_2 and $HSiCl_3$).
2. Diffusion of nickel metal into the metastable silicide phase and chemical reaction leading to the thermodynamically stable product.

Step 1, the formation of Ni_2Si from NiSi was investigated by isothermal X-ray powder diffraction at 390°C. By means of this method the reaction can be followed only in a small temperature range. At 370°C, the rate is too slow to observe reliable changes during a few hours. At 410°C, Ni_2Si and Ni are formed within a few minutes.

Peaks, which are not in coincidence with other peaks, were integrated (pseudo-Voigt2) and their area plotted as a function of time. For different NiSi peaks ([211] and [020]), the obtained kinetic parameters were consistent. Data of $NiCl_2$ was obtained from the single [112]-peak. In case of accordance of NiSi [001] with Ni [100] and NiSi [112] with the peak of an intermediately formed phase, referred as [Ni–Si], the derived function of NiSi was used to correct the peak areas of the overlapping peaks. The curves are shown in Fig. 6 (upper picture) [11]. We
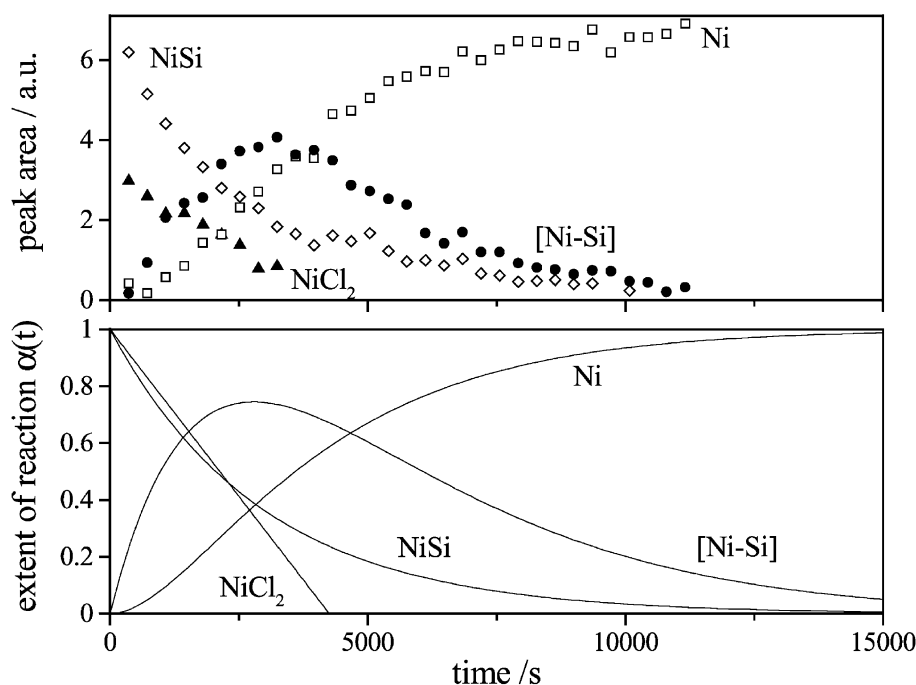
Fig. 6. Kinetics of reaction (10). Peak area as function of time (upper figure) [11], and calculated extent of reaction from the kinetic data in Table 2.

have assumed that the molar ratio of Ni and Si in the intermediate phase is 2:1, derived from the observation that the intermediate phase is later rapidly and fully converted into Ni_2Si. A formalized kinetic rate model of two first-order consecutive reactions, according to Eq. (11), is applied. $NiCl_2$ reacts according to a zero-order rate law (Eq. (12)). The model fully mathematically explains the interdependence between the reaction of NiSi and HCl, which is formed by the reduction of $NiCl_2$. The results are given in Table 2 and Fig. 6.

$$NiSi \xrightarrow{k_1} 1/2[Ni–Si] \xrightarrow{k_2} Ni \qquad (11)$$

$$NiCl_2 \xrightarrow{k'} Ni \qquad (12)$$
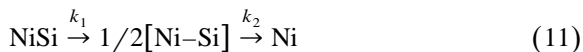
The final diffraction pattern of that isothermal investigation shows Ni and some unknown peaks remaining from the intermediate phase. Similar experiments as well as XRD-studies of stepwise heating of $NiSi/NiCl_2$ mixtures (molar ratio 7:2) gave some diffraction pattern having unknown reflexes. Based on the present knowledge, we suppose that the existence of all these phases are kinetically determined and not related to a defined structure. They

might be formed by a hindered relaxation of the collapsing or reorganizing nickel silicide lattice during the removal of silicon. On the basis of the presented results, we suppose that the appearing high mobility of silicon (nickel was found to be the more mobile species with a 10 times greater mobility than Si [7,8]) results from the motion of silicon to the surface and the fast diffusion of nickel atoms of the NiSi phase backwards into the bulk under formation of Ni_2Si.

Table 2
Kinetic parameters evaluated from the isothermal X-ray powder diffraction study of reaction (10). Rate constants k_1 and k_2 are referred to Eq. (11) and k' to Eq. (12). $(A(NiSi)_0$ and $A(NiCl_2)_0$ are the peak areas of the diffraction peaks of NiSi and $NiCl_2$ at time $t = 0$)

Component	$k_1 \cdot 10^4 / s^{-1}$	$k_2 \cdot 10^4 / s^{-1}$	$A(NiSi)_0$ /a.u.
NiSi	3.38 ± 0.13	–	6.46 ± 0.19
[Ni–Si]		3.81 ± 0.16	6.95 ± 0.24
Ni		3.48 ± 0.43	5.09 ± 0.11

component	$k' \cdot 10^4 / s^{-1} \cdot$ a.u.	–	$A(NiCl_2)_0$ /a.u.
$NiCl_2$	7.44 ± 0.50	–	3.16 ± 0.10

Table 3
Thermodynamic data and experimental results of the reaction between Si and nickel halogenides ($\Delta_R H$ enthalpy of reaction, $\lg(K)$ equilibrium constant)

NiX_2	$\Delta_R H$ (298 K)/ kJ · mol^{-1}	$\lg(K)$ at 298 K	Start temperature of the reaction/°C	Isolated compounds
NiF_2	−470.20	91.41	270...300	NiSi, Si, Ni
$NiCl_2$	−222.76	48.02	400...420	Ni_2Si, NiSi, Si
$NiBr_2$	−162.42	37.43	> 500	Ni_2Si, Ni_3Si_2, NiSi, Si
NiI_2	−124.77	31.07	Decomposition of NiI_2	–

Due to the strongly negative formation enthalpies of the silicides, reaction (3) has a higher enthalpy of reaction than reaction (2). Reaction (3) was adapted to the Ni–Si system (Eq. (13)) in order to obtain comparable results.

$$3Si(s) + 2NiX_2(s) \rightarrow 2NiSi(s) + SiX_4(g),$$
$$X = F, Cl, Br, I \qquad (13)$$
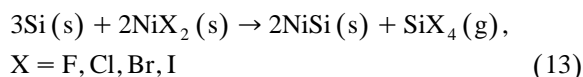
The educts were pressed to pellets and heated up in an argon flow or under argon atmosphere in a closed system. The reactivity of nickel halogenides decreases in the order $NiF_2 > NiCl_2 > NiBr_2$, as well as the reaction enthalpies, whereas the starting temperatures of the process is increasing in this order (Table 3). A dependence of the formed products on the used halogenide was found. But a selective phase production is not yet possible, neither under argon flow nor in a closed system. The high reaction enthalpies lead to a drastic uncontrollable increase of the process temperature and the reaction is accelerated. The isolated product mixtures are evidence for rapid, incomplete and uncontrolled reactions.

5. Discussion

In all these discussed solid–gas reactions, the persistent presence of the corresponding gas atmosphere is a necessary precondition to realize a rapid and selective phase formation. There is a steady-state relation between solid and gaseous phases in the flow reactor or a closed system, maintaining the gases formed during the reaction. Processes based on reaction (13) are strongly exothermic and faster than that one based on reaction (10). Via the solid–gas reactions, silicide phases are faster formed than from solid-state reactions known.

At the end, two conclusions should be mentioned. The kinetic data are pointing to a very high mobility of silicon in the investigated nickel silicide phases. In contrast, it had been shown by several investigations that in Ni–Si diffusion couples or thin film experiments Ni is the more mobile species (e.g. Refs. [7,8]).

Furthermore, it should be kept in mind that in our experiments NiSi reacts to Ni_2Si. From all that we suppose, that while silicon is removed from NiSi, Ni diffuses backwards into the NiSi, and forms Ni_2Si. (This Ni_2Si–NiSi formation sequence by the diffusion of Ni had been proven earlier [7,8].) It might be that the mobility of either Si and/or Ni is enhanced by the presence of chlorine at the surface, as well as in the Ni_2Si layer.

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