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Thermodynamic Consideration of Si–N and Si–H–N Systems for Silicon Nitride Powder Production in Thermal Plasma

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Abstract: The results of equilibrium composition and total enthalpy computation in the temperature range of 1000–6000 K and at 1 bar for Si–N and Si–H–N systems are presented in the paper. These data enable temperature and energy parameters determination and optimization of the process for ultrafine silicon nitride powder production, in which silicon powder evaporation in a nitrogen thermal plasma is followed by quenching with nitrogen or ammonia.

1 INTRODUCTION

Silicon nitride is a basic material for high-temperature-resistant ceramic materials due to its excellent high temperature physical, chemical and mechanical properties. For sintering high quality ceramic parts it is necessary to use chemically pure powder with uniform submicron particles and high specific surface area. Synthesis of silicon nitride powder with predescribed properties is the first, but very important step in advanced ceramics production.

Thermal plasma is a high-temperature mixture of gases, ions and electrons characterized by high energy densities and relatively high values of thermal conductivity and transport properties. The advantage of thermal plasma is the possibility of obtaining any desired chemical composition and the independent choice of temperature level. Materials exposed to thermal plasma will be readily heated, evaporated and decomposed into free atoms, ions and electrons. Quenching of these highly excited species under 'controlled conditions' results in nucleation and growth of ultrafine powders and crystals.

Thermodynamic calculations of the equilibrium composition of the system help us to determine temperature and energetic conditions for evaporation, decomposition or quenching necessary to obtain the desired products.

This paper presents thermodynamic considerations of Si–N and Si–H–N systems for plasma synthesis of silicon nitride powders. The results enable determination and optimization of mass, temperature and energy parameters of the process.

2 COMPUTATION METHOD

Thermodynamic methods used for chemical equilibrium composition computation are highly efficient, especially in low-temperature thermal plasma ($T < 6000$ K) at atmospheric or lower pressure. Thermal plasmas follow ideal gas behaviour because: (1) the temperature is sufficiently high (1000–6000 K) at relatively low pressure, and (2) concentration of ions and electrons is small.

Two basic approaches are used to model the thermodynamic equilibria of systems which undergo chemical reactions. The first, as used here, is based on the Mass Action Law.[1] The second is based on the minimization of free enthalpy (Gibbs free energy).[2]

The first step in the thermodynamic modelling of the chemical equilibria involves a decision about the number of gas and condensed (solid or liquid) phase species to be considered. Let this number be m, the number of dense (solid and liquid) phase species be f and the number of atomic species be q, then $m-q$ mass action equations will determine equilibrium composition. In other words, $m-q$ equilibrium constants pertain. The equilibrium constants are usually specified for the decomposition reactions to the constituent atoms; all the equations being independent, such that

$$K_j(T) = \prod_{i=1}^{q} \frac{p_i^{a_{ij}}}{p_j} (j = 1, 2, ... m - q) \tag{1}$$

where p_i are the partial pressures of the atomic species, p_j are the partial pressures of the molecular species, a_{ij} are the stoichiometric coefficients of decomposition reactions, and $K_j(T)$ are the mass action constants for decomposition into the atoms.

The Mass Action Law in the form of the Saha equation[3]

$$\frac{n_e n_{ix}}{n_i} = 2 \frac{Z_{ix}}{Z_i} \frac{(2\pi m_e)^{3/2}(kT)^{3/2}}{h^3} e^{(-E_i/kT)} \tag{2}$$

is used for thermal ionization. Here n_e, n_{ix} and n_i are the density of electrons, ions and atoms, respectively, Z_i and Z_{ix} are the partition functions of atom and corresponding (singly ionized) ion, m_e is the electron mass, k is the Boltzmann constant, h is the Planck's constant, T is the gas temperature, and E_i is the first ionization energy of atom i.

In the case of condensed (solid or liquid) substances that do not form solid solutions, the application of the mass action law, based on the constant saturation pressure (p_l^c) above the condensed phase at a fixed temperature (T), f other equations occur. These are of the form

$$K_l^c(T) = p_l^c \ (l = 1, 2, ..., f) \tag{3}$$

where subscript l indicates either atomic or molecular chemical species.

For an ideal gas mixture, Dalton's law is introduced in the form

$$\sum_{l=1}^{g} p_l = p \tag{4}$$

where s is the number of gas species and p is total pressure of the mixture.

In order to close the system of equations, the $q-1$ mass balance equations are included

$$\frac{\sum_{l=1}^{g} a_{ol} p_l + \sum_{l=1}^{f} a_{ol} p \nu_l^c}{\sum_{l=1}^{g} a_{dl} p_l + \sum_{l=1}^{f} a_{dl} p \nu_l^c} = \frac{O}{D} \tag{5}$$

where a_{ol} and a_{dl} are the numbers of o and d atomic species comprising product molecule l, ν_l^c is the ratio of number of moles of condensed phase of constituent l to total number of moles in gas mixture, O and D are the o and d atomic species content in the reactants, respectively.

For the decomposition reaction defined by the stoichiometric equation

$$A_a B_b C_c \cdots \rightleftharpoons aA + bB + cC + \cdots \tag{6}$$

its equilibrium constant, defined by eqn (1), is related to mole free enthalpies (Gibbs free energies) by the relationship

$$\begin{aligned} RT lnK_j(T) &= -\Delta_j G(T) = \\ &- \{[aG(A,T) + bG(B,T) + cG(C,T) + \cdots] \\ &- G(A_a B_b C_c \cdots, T)\} \end{aligned} \tag{7}$$

where $\Delta_j G(T)$ is free enthalpy change for reaction (6) and R is the universal gas constant. If the modified free enthalpy of constituent i is defined as[4]

$$\begin{aligned} \Phi_i(T) &= -[G_i(T) - H_i(0)]/T = \\ & S_i(T) - [H_i(T) - H_i(0)]/T \end{aligned} \tag{8}$$

the equilibrium constant $K_j(T)$ from eqn (1) can be calculated from the relationship

$$R lnK_j(T) = \Delta_j \Phi(T) - \Delta_r H_j(0)/T \tag{9}$$

where $\Delta_r H_j(0)$ is a chemical reaction enthalpy change at $T = 0$ K.

The total enthalpy of the system, H_s at temperature T, is calculated by adding an enthalpy of constituents (gaseous and condensed)

$$H_s(T) = n_g \left[\sum_{l=1}^{g} \nu_l H_l(T) + \sum_{l=1}^{f} \nu_l^c H_l^c(T) \right] \tag{10}$$

where n_g is the total number of moles in gaseous phase, ν_l is the mole fraction of gas constituent l, H_l (kJ/mol) and H_l^c (kJ/mol) are mole enthalpies of gas and condensed phase of constituent l, respectively, defined by relationship

$$\begin{aligned} H_l(T) &= -T^2 \left[\partial(G/T)/\partial T \right]_{p,\nu_l} = \\ & T^2 \left[\partial \Phi_l / \partial T \right] + \Delta_f H_l(0) \end{aligned} \tag{11}$$

$\Delta_f H_l(0)$ is the heat of formation of constituent l, from elements at standard state, for temperature $T = 0$ K.

The polynomial coefficients of the temperature dependence of modified free enthalpies (Gibbs free energies Φ_i, Φ_l), chemical reaction enthalpy change [$\Delta_r H_j(0)$] and the heat of formation (from elements at standard state and temperature 0 K) of constituent l [$\Delta_f H_l(0)$, $\Delta_f H_k^c(0)$], are taken from the literature.[4] These data[4] are equivalent to those in Ref. 5.

The system of equations (1)–(5) is a non-linear system of algebraic equations which is usually solved by iteration, starting from a selected set of initial values of partial pressures, using Seidel's,[6] Newton–Raphson's[6] or some other method. If Newton–Raphson's method is used the system of equations must be linearized first. This may be achieved either by a Taylor expansion of an unknown partial pressure, in which the second and higher order terms may be neglected, or by taking the logarithm of the set of equations (1)–(5) and then solving for the logarithms of the unknown quantities.

For systems with condensed phases, irrespective of the method used, there are cases where convergence problems may be encountered. In the work reported here the straightforward iterative method was used to obtain the solution. Only the initial set of partial pressures for the major constituents are specified. Solution progresses from the lower temperature (1000 K) at which one, two or three species exist in a condensed phase (at that temperature their partial pressures equal their saturation pressure). Moreover, in the first iteration at the lowest temperature, the partial pressure deemed to be highest is accepted, and, in all following steps, it is determined using eqn (4). The temperature increment was 25 K. The set of values obtained for the major constituents at a previous temperature becomes the input for the first iteration at the next, higher temperature level.

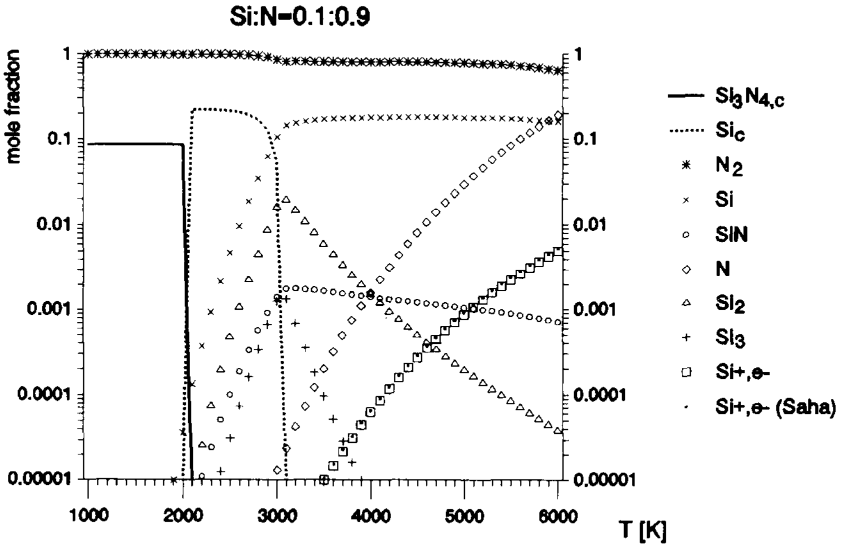

Fig. 1. Equilibrium composition of the Si–N system for atomic ratio Si:N = 0.1:0.9.

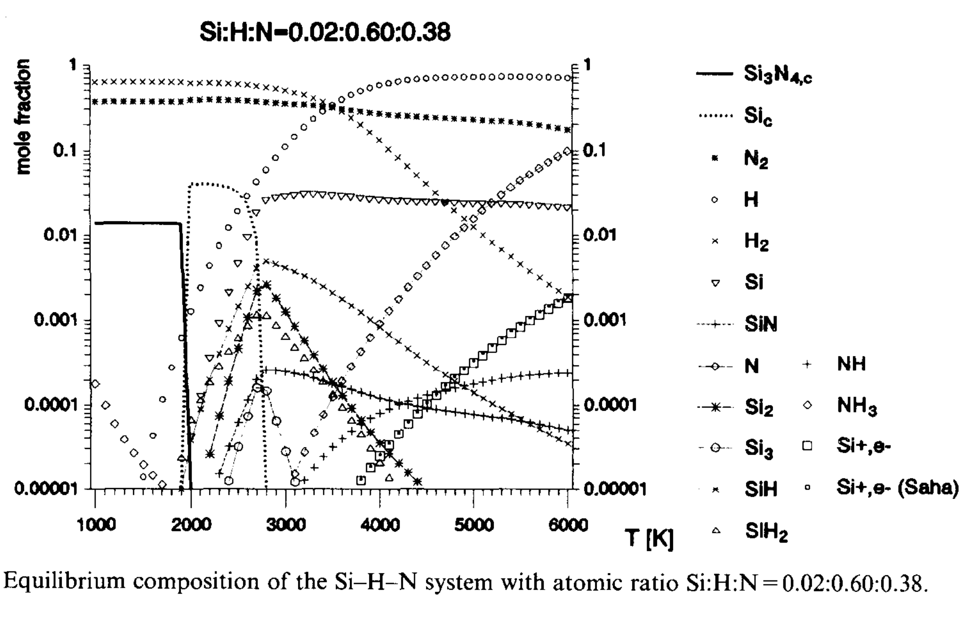

Fig. 2. Equilibrium composition of the Si–H–N system with atomic ratio Si:H:N = 0.02:0.60:0.38.

Regions within which the system of equations, (1)–(5), requires modification in order to accommodate the appearance or disappearance of any species in the condensed phase are readily observed in the composition diagrams (Figs 1 and 2). The computation condition for the appearance of constituent l (at any temperature) in the condensed phase is $p_l > K_l^c$; the condition for disappearance of condensed phase of constituent l is $\nu_l^c < \epsilon$, where ϵ has an arbitrary small value specified in advance (ϵ was 1×10^{-6}).

3 RESULTS AND DISCUSSIONS

The temperature dependence of the equilibrium composition for the Si–N system with atomic ratio Si:N = 0.1:0.9 is given in Fig. 1 and for the Si:H:N system with atomic ratio Si:H:N = 0.02:0.60:0.38 in Fig. 2.

Two condensed phases are possible: silicon nitride ($Si_3N_{4,c}$) and silicon (Si_c).

The silicon nitride powder ($Si_3N_{4,c}$) can exist for $T < 2000$ K (Figs 1 and 2). In the temperature range from 2000–3100 K (Fig. 1) or between 2000 and 2800 K (Fig. 2), Si-droplets (Si_c) can be condensed, and this region must be passed quickly if we want to synthesize pure silicon nitride powder.

All other species are in the gaseous state. A small mole fraction of Si^+ ions and electrons exist at higher temperature only (less then 0.4% for temperature $T = 6000$ K). The mole fraction of Si^+ ions (and electrons) was calculated in two ways: (1) by using the Saha equation (2) in which the ratio of partition function for Si^+ and Si is $Z_{ix}/Z_i = 9/6$ (from Refs 3 and 7), assuming quasi-neutrality ($n_e = n_{Si+}$), these results represented in Figs 1 and 2 are assigned as Si^+, e^- (Saha); and (2) by using equation analogue to eqn (1) for decomposition of Si atom to Si^+ and an electron for the data from Ref. 4 (Si^+, e^- in Figs 1 and 2). These two approaches give practically the same results, as can be seen from Figs 1 and 2.

The temperature dependence of total enthalpy (per one mol*) for the Si–N system is presented in Fig. 3; for the Si–H–N system in Figs 4–8 (constant fractions of H in one mol* of the system, in each figure). One mol* is defined as the quantity of the system, which consists of one gram atom of all atomic species, in total. (For example, 1 mol* of the system in Fig. 2 consists of 0.02 gram atoms of Si + 0.60 gram atoms of H + 0.38 gram atoms of N.) The enthalpy of nitrogen plasma is also shown (curve for Si:N = 0.00:1.00 in Fig. 3 and curve for Si:H:N = 0:0:1 in Figs 4–8). The curve Si:H:N = 0:0.75:0.25 (for the enthalpy of ammonia plasma) is also presented, see Figs 4–8. In the temperature range from 1000 to 2000 K the influence of atomic fraction of H in the system on the total enthalpy value, H_s, can be neglected due to the small enthalpy difference between H_2 and N_2 (in this temperature range, the gas phase consists mostly of H_2 and N_2; see Fig. 2).

Presented results indicate technological steps in the plasma chemical process for silicon nitride powder synthesis from Si powder as a precursor. In the first step, silicon powder injected in nitrogen plasma is evaporated: as a result of the evaporation process the Si–N system cools. In the second step, the system must be quickly cooled down to a tem-

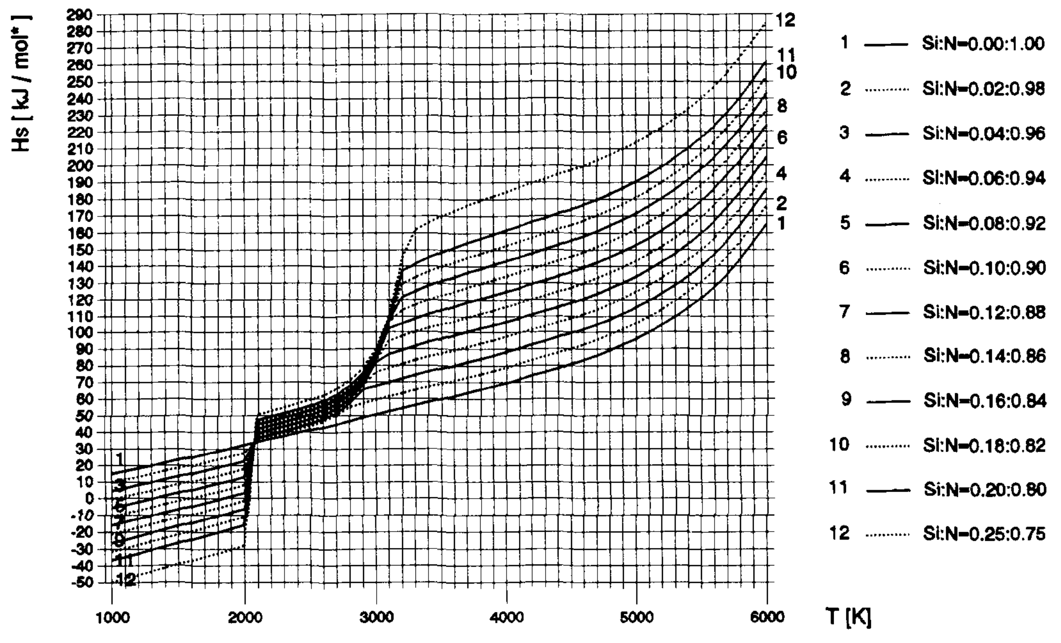

Fig. 3. Temperature dependence of enthalpy for the Si–N system at $p = 1$(bar).

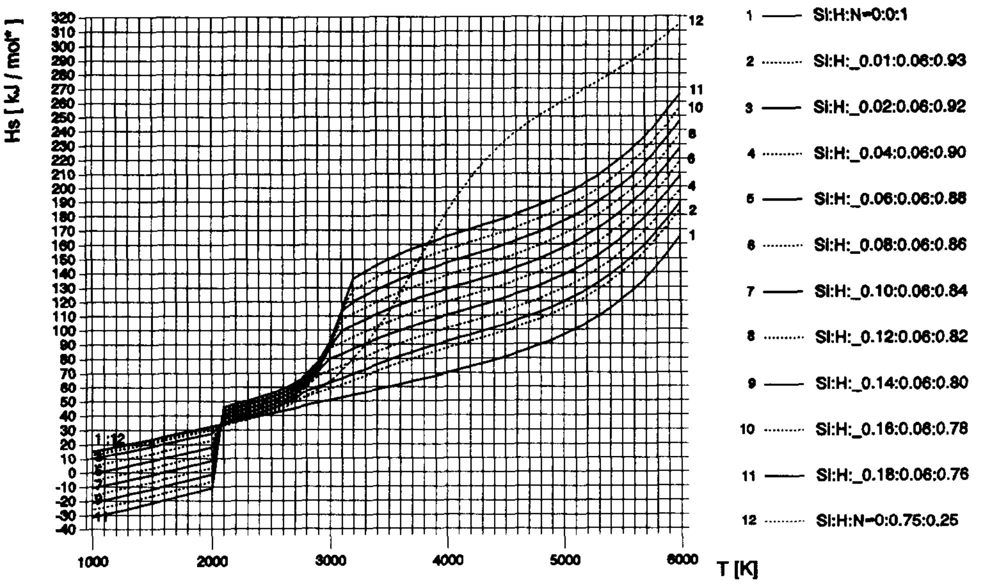

Fig. 4. Temperature dependence of enthalpy for the Si–H–N system at $p = 1$(bar) for atomic fraction of H: 0.06.

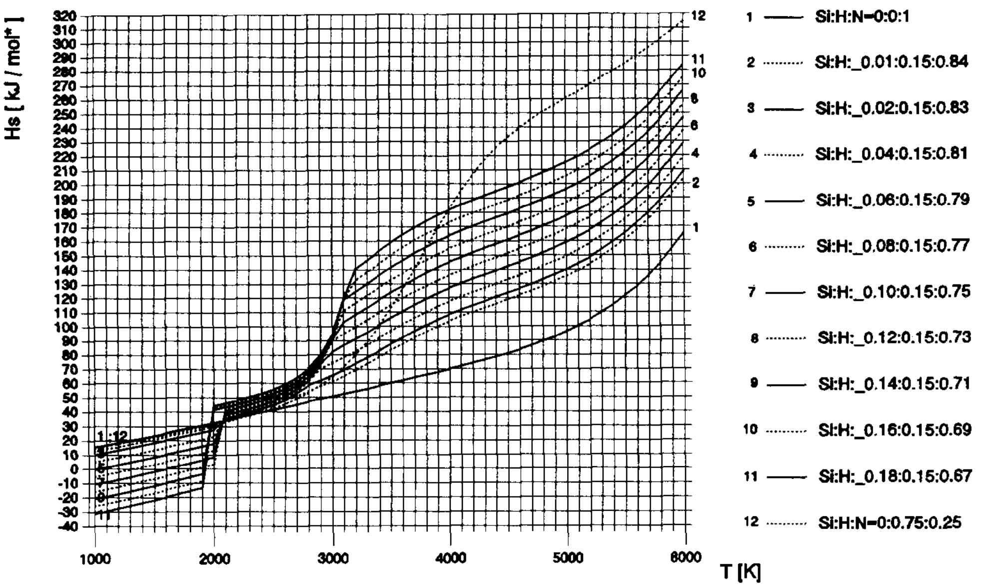

Fig. 5. Temperature dependence of enthalpy for the Si–H–N system at $p = 1$(bar) for atomic fraction of H: 0.15.

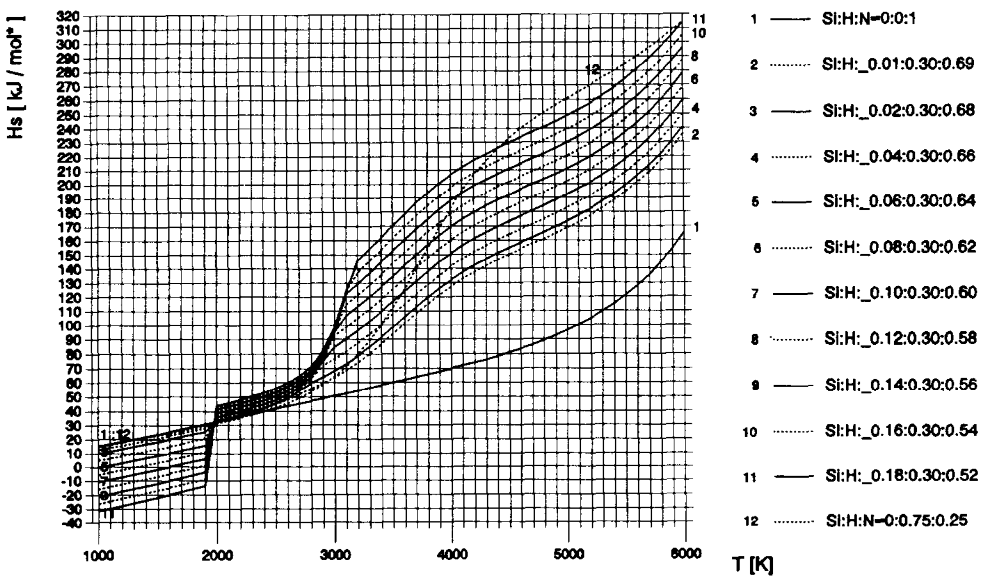

Fig. 6. Temperature dependence of enthalpy for the Si–H–N system at $p = 1$(bar) for atomic fraction of H: 0.30.

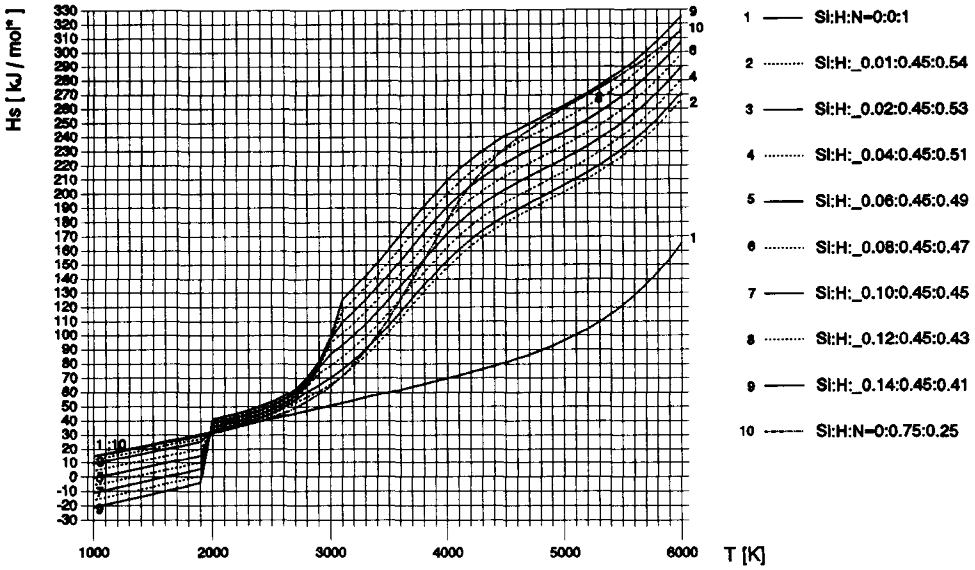

Fig. 7. Temperature dependence of enthalpy for the Si–H–N system at $p = 1$(bar) for atomic fraction of H: 0.45.

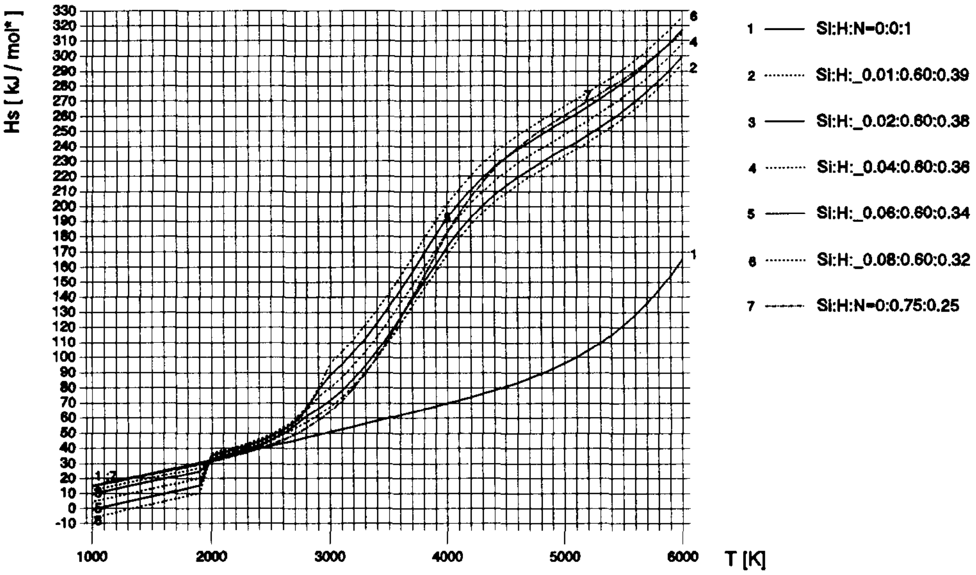

Fig. 8. Temperature dependence of enthalpy for the Si–H–N system at $p = 1$(bar) for atomic fraction of H: 0.60.

perature between 1000 and 2000 K (see Figs 1 and 2) in which the deposition of the silicon nitride powder is possible. Temperature and energy parameters calculations for silicon nitride powder production processes, based on presented results, are illustrated through an idealized example.

Example. (It is presumed that there are no heat losses to surroundings.) Suppose we inject 0.1 mol of Si (at temperature $T = 298.15$ K) to 0.9 mol* of nitrogen plasma, then we will obtain the system with atomic content Si:N = 0.1:0.9. If the temperature of the nitrogen plasma is $T_1 = 5700$ K, from Fig. 3 (curve no.1, for Si:N = 0.00:1.00) we can find that the enthalpy of nitrogen plasma (mixture of N_2 and N) is $H_{s,1} = 136$ kJ/mol*. The inlet enthalpy of Si is $H_{\text{Si,in}} = 3.217$ kJ/mol.[4] The enthalpy of the system after the evaporation of Si will be:

$$H_{s,2} = 0.1 \cdot H_{\text{Si,in}} + 0.9 \cdot H_{s,1} = \\ 0.1 \cdot 3.217 + 0.9 \cdot 136 = 122.72\,\text{kJ/mol}^*$$

For this enthalpy value in Fig. 3 (curve no.6 for Si:N = 0.1:0.9) one can find that the corresponding temperature of the system is $T_2 = 4250$ K.

By quenching with supplementary nitrogen or ammonia, the temperature of the system must be reduced to $T < 2000$ K (Fig. 1), in which it is possible to obtain pure silicon nitride powder.

1. If we inject 0.425 mol of cold nitrogen, whose enthalpy at $T = 298.15$ K is $H_{\text{N2,in}} = 8.67$ kJ/mol,[4] to 0.15 mol* of the system Si:N = 0.1:0.9, the new atomic content of the obtained system is Si:N = 0.015:0.985. The enthalpy of this system will be:

Table 1. Saturation ratio $S_{Si} = p_{Si} / p_{Si,sat}$

T (K)	2100	2200	2300	2400	2500	2600	2700
$S_{Si}(1)$	23.6	14.6	8.9	5.5	3.3	1.9	1.2
$S_{Si}(2)$	25.2	15.4	9.5	5.8	3.5	2.1	1.3

Table 2. Saturation ratio $S_{Si3N4} = p_{Si}{}^3 p^4{}_N / K_{Si3N4}$

T (K)	$S_{Si3N4}(1)$	$S_{Si3N4}(2)$
1100	1.35×10^{35}	2.66×10^{34}
1200	3.40×10^{29}	6.64×10^{28}
1300	6.34×10^{24}	1.23×10^{24}
1400	5.72×10^{20}	1.10×10^{20}
1500	1.81×10^{17}	3.48×10^{16}
1600	1.59×10^{14}	3.02×10^{13}
1700	3.18×10^{11}	6.00×10^{10}
1800	1.26×10^{9}	2.35×10^{8}
1900	8.73×10^{6}	1.61×10^{6}
2000	9.57×10^{4}	1.75×10^{4}
2100	1.52×10^{3}	2.74×10^{2}
2200	3.26×10^{1}	5.78×10^{0}
2300	8.78×10^{-1}	1.54×10^{-1}

$$H_{s,3} = 0.15 \cdot H_{s,2} + 0.425 \cdot H_{\mathrm{N2,in}} =$$
$$0.15 \cdot 122.72 + 0.425 \cdot 8.67 = 22.09\,\mathrm{kJ/mol}^*$$

In Fig. 3 for Si:N = 0.015:0.985 (above curve no.2) and for enthalpy values 22.09 kJ/mol*, we can find that the corresponding temperature of the system is $T_3 = 1550$ K.

2. If we inject 0.2 mol of the cold ammonia, the enthalpy[4] $H_{\mathrm{NH3,in}} = -28.907$ kJ/mol at $T = 298.15$ K, to 0.2 mol* of the system Si:N = 0.1:0.9, the new atomic content of the obtained system will be Si:H:N = 0.02:0.6:0.38. The enthalpy of this system will be

$$H_{s,3} = 0.2 \cdot H_{s,2} + 0.2 \cdot H_{\mathrm{NH3,in}} =$$
$$0.2 \cdot 122.72 + 0.2(-28.907) = 18.76\,\mathrm{kJ/mol}^*$$

In Fig. 8 (curve no.3 for Si:H:N = 0.02:0.6:0.38) for enthalpy values 18.76 kJ/mol*, we can find that the corresponding temperature of the system is $T_3 = 1550$ K.

It is obvious that the example shown here needs a few iterations. Only the last is presented here.

From equilibrium consideration it is not possible to make any conclusion about silicon nucleation and condensation during the quenching process. A thermodynamic approach[8] can be used to derive an expression for the equilibrium vapour pressure p_d, of a liquid drop of diameter d_p

$$\ln\frac{p_d}{p_s} = \frac{4v_{\mathrm{mol}}\,\sigma}{d_p RT} \qquad (12)$$

where p_s is the vapour pressure above a flat surface, σ is the surface tension and v_{mol} is the molar volume of the liquid. Equation (12) indicates that the vapour pressure over a small drop is considerably greater than that over a plane surface (the Kelvin effect). For homogeneous nucleation, which will occur in the system without the foreign particles, the Kelvin effect sets a lower limit on the droplet size (silicon in this case) that can serve as condensation nuclei. According to the Kelvin relation (12), the higher the saturation ratio, the smaller the radius of the droplet that can serve as a stable nucleus for condensation. Wilson, in his Nobel Lecture, 1927,[9] reported that in the experiments with water vapour, it was found that the critical saturation ratio for homogeneous nucleation is about eight. Similar results were found with other condensable vapours, but the value of the critical saturation ratio changes with the nature of the vapour. In the absence of the other experimental data, it is usual to take the value of supersaturation to be about 10, for rough estimation of stable nucleus formation. Based on this assumption, it can be shown that with the fast cooling process (quenching) in temperature range between 2800 (3000) and 2000 K (Figs 1 and 2), silicon nucleation can be avoided, and thus pure silicon nitride powder obtained.

For the previous example, the values of the supersaturation ratio are calculated from the equilibrium composition of the system with the assumption that there is no condensation of silicon droplets and no deposition of solid silicon nitride ($\mathrm{Si_3N_{4,c}}$), i.e. that only the gaseous phase exists in the system. Results are presented in Tables 1 and 2. p_{Si} (in Tables 1 and 2) is the partial pressure of Si in the system calculated under the assumption that there is no condensation of silicon and no deposition of silicon nitride; $p_{\mathrm{Si,sat}}$ is the saturation pressure of silicon at a plane surface. Partial pressure of atomic nitrogen p_{N} (Table 2) is calculated under the assumption that there is no deposition of solid silicon nitride in the system; K_{Si3N4} is the equilibrium constant for silicon nitride as defined by eqn (1).

As can be seen from Table 1, value $S_{\mathrm{Si}}(1)$ for the system Si:N = 0.015:0.985 (the first part of the given example) shows that the condition for formation of a stable nucleus for homogeneous condensation, exists only in the narrow temperature range from 2300 to 2100 K, i.e. fast cooling (quenching) is necessary in this temperature range to prevent the condensation of silicon droplets. Similarly for the system Si:H:N = 0.02:0.60:0.38 for the second part of the given example (see value $S_{Si}(2)$ from Table 1). On the other hand, when the temperature decreases from 2100 to 1100 K, the supersaturation ratio ($S_{\mathrm{Si3N4}}(1)$ for the system Si:N = 0.015:0.985 and $S_{\mathrm{Si3N4}}(2)$ for the system Si:H:N = 0.02:0.60:0.38, in Table 2), increases quickly to enormous values, and there is no doubt that fast deposition of silicon nitride powder occurs as the temperature of the system decreases below 2100 K.

The possibility of avoiding the nucleation of Si droplets under controlled conditions of quenching, shown by the presented thermodynamic analysis, is experimentally proved by different authors.[10–13] Quenching can be realized by injection of cold nitrogen or ammonia flow, although the second is preferable, because much less ammonia is required, as shown by the example.

4 CONCLUSION

Thermodynamic computation (of the equilibrium composition and total enthalpy behaviour) of chemical reactive system is useful and essential for the thermal plasma synthesis process, as is shown on the Si–N and Si–H–N systems for the production of silicon nitride powder in nitrogen plasma from silicon powder as a precursor. Results of calculations enable:

- — the optimal plasma process route to be determined,
- — the probability of individual reaction occurring as stages of a whole process to be evaluated,
- — the temperature and energy parameters of the plasma process to be determined and optimized,
- — to cut down experimental work and decrease the cost of investigations.

The application of the thermodynamic method is highly efficient, especially in the temperature range of 1000–6000 K at relatively low pressure (as in the present case, at ≈ 1 bar). Thermal plasmas follow the ideal gas behaviour because: (1) the temperature is sufficiently high (1000–6000 K) at relatively low pressure, and (2) the concentration of ions (and electrons) is small.

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