

THERMODYNAMICS OF SILICON NITRIDE

Standard molar enthalpy of formation of amorphous Si_3N_4 at 298.15 K

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Abstract

The standard molar enthalpy of formation $\Delta_f H_m^0 = -760 \pm 12$ kJ for amorphous silicon nitride $\alpha\text{-Si}_3\text{N}_4$ has been determined from fluorine combustion calorimetry measurements of the massic energy of the reaction: $\alpha\text{-Si}_3\text{N}_4(s) + 6\text{F}_2(g) = 3\text{SiF}_4(g) + 2\text{N}_2(g)$. This value combined with $\Delta_f H_m^0 = -828.9 \pm 3.4$ kJ for $\alpha\text{-Si}_3\text{N}_4$ indicates that determined for the first time molar enthalpy change for the transition from amorphous to α -crystalline form $\Delta_{\text{tr}} H_m^0 = 69 \pm 13$ kJ is very evident, in spite of its large uncertainty range resulting from impurity corrections.

Keywords: fluorine bomb calorimetry, silicone nitride, standard enthalpy of formation

Introduction

Silicon is not only the second most common element after oxygen in the Earth's crust but also a basic component of some 'high-tech' materials used in many advanced technologies. Silicon nitride Si_3N_4 , one of the most important materials containing silicon, was known for almost 140 years [1], but in relatively recent times has been recognized and used as an engineering ceramic with many new applications [2, 3]. Silicon nitride occurs in different amorphous forms which, in general, are not very well characterized and in two hexagonal crystalline modifications, $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$. Amorphous Si_3N_4 is produced mainly by pyrolysis of polysilazanes and thermal decomposition of other polymer ceramic precursor materials. On heating the amorphous form converts to crystalline modification $\alpha\text{-Si}_3\text{N}_4$ [4], which then can transform to $\beta\text{-Si}_3\text{N}_4$. Although silicon nitride is such a prominent material that its thermodynamic properties were not so consistent as its importance demands. For example, in literature survey and critical assessment given in the reference book of Gurvich *et al.* [5], collected data for the standard molar enthalpy of formation $\Delta_f H_m^0$ (Si_3N_4 , 298.15 K) were scattered from -621 to -842 kJ.

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That was the reason why in the last few years thermodynamic properties of silicon nitride became the object of calorimetric fluorine combustion studies conducted by O'Hare *et al.* [6, 7]. The standard molar enthalpies of formation of α and β forms at $T=298.15$ K have been determined: $\Delta_f H_m^0(\alpha\text{-Si}_3\text{N}_4) = -828.9 \pm 3.4$ kJ and $\Delta_f H_m^0(\beta\text{-Si}_3\text{N}_4) = -827.8 \pm 2.5$ kJ and also the molar enthalpy change for the α to β transition, which found to be negligible -1 ± 4 kJ within the uncertainties. This work was the continuation of previous investigations [6, 7]. Briefly, its objective was to determine massic energy of combustion of $\alpha\text{-Si}_3\text{N}_4$ in fluorine, and from this quantity, to derive standard enthalpy of formation of amorphous silicon nitride, and then on the basis of standard molar enthalpies of formation of amorphous and α forms to estimate the molar enthalpy of transition from amorphous to α -crystalline form.

The measurements of the energy of the combustion reaction between $\text{F}_2(\text{g})$ and Si_3N_4 were performed in a high-precision fluorine bomb calorimeter at National Institute of Standards and Technology (Gaithersburg, Maryland, USA). Fluorine bomb calorimetry has been effectively used in investigations of inorganic substances that cannot be combined easily with conventional calorimetric reagents such as high-pressure oxygen or mineral acids. Our previous experience has shown that crystalline forms of silicon nitride reacted readily with fluorine and it was expected that amorphous Si_3N_4 would behave in the same way.

Experimental

Materials

Amorphous Si_3N_4 was prepared in Pulvermetallurgic Laboratory in Stuttgart Max Planck Institute by pyrolysis of polyvinylsilazane precursor VT50 under flowing NH_3 atmosphere. Pyrolysis was conducted in a quartz tube heated by a tube furnace. The temperature was raised from 323 to 1323 K with a heating rate 25 K h^{-1} and then kept at 1323 K over a period of 4 h. Thereafter, the product was cooled down at the rate 300 K h^{-1} . To protect the specimen of amorphous Si_3N_4 from surrounding atmosphere, the sample was kept in a flask with a sealed valve and during calorimetric experiments at NIST was stored in the glovebox purged by recirculating nitrogen purified of O_2 and H_2O by continuous passage over finely divided copper and molecular sieves. High-purity $\text{F}_2(\text{g})$, prepared by distillation (Air Products) before use was passed through a column filled with NaF to remove any traces of HF.

The sample of amorphous silicon nitride was analyzed in Pulvermetallurgic Laboratory for the amount of Si (by optical emission spectroscopy with inductively coupled plasma source and Fourier transform infrared spectroscopy), total amount of N and for the presence of O, C and H. However, before performing fluorine combustion experiments the analysis for the amount of O, C and H in amorphous $\text{-Si}_3\text{N}_4$ specimen was repeated (by LECO Corporation, St. Joseph, MI, USA). The reason for that was precaution which can be justified by the following statement written in Gmelin's Handbook [8]: 'Oxygen values sometimes deviated considerably from a manufacturer's specifications, perhaps due to variations in water content and ageing

during storage'. The analysis performed by LECO was the following: oxygen was determined by inert gas fusion with infrared detection; hydrogen by inert gas fusion and thermal conductivity; carbon, by high temperature combustion with infrared detection. These results were used further for the calculation of the impurity corrections. Amorphous silicon nitride materials normally contain few mass% of oxygen, and this content is an essential factor in all its reactions. According to the detailed discussion presented in a previous paper [6], it was assumed that impurities of C, H, and O are present respectively as SiC, NH₃ and SiO₂. The analytical results are collected in Table 1 and their consistence seems to be confirmed by the fact, that the mass fractions of all elements summarized together gave the result equal to 1, within the uncertainty limits. Next, in Table 2 it is presented that, as it is required for stoichiometric Si₃N₄, the value of molar amount of substance ratio $n(\text{Si})/n(\text{N})$ is close to 3/4, within the uncertainties.

Table 1 Analytical results for α -Si₃N₄ sample; mass fraction is denoted by w

Element	$w \cdot 10^2$	Assumed phase
Si	56.42±0.55	Si ₃ N ₄ , SiC, SiO ₂
N	37.70±1.09	Si ₃ N ₄ , NH ₃
O	5.155±0.135	SiO ₂
H	0.84±0.01	NH ₃
C	0.294±0.015	SiC
Total	100.4±1.23	

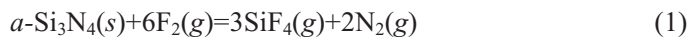
Table 2 The ratio $n(\text{Si})/n(\text{N})$ for α -Si₃N₄; w denotes mass fraction of Si and N combined as impurities and silicone nitride

Impurity	$w \cdot 10^2$ (Si in impurity)	$w \cdot 10^2$ (N in impurity)
SiC	0.687±0.035	
SiO ₂	4.524±0.118	
NH ₃		3.891±0.014
Total	5.211±0.123	3.891±0.014
$w(\text{Si})$ as Si ₃ N ₄ = $10^{-2} \{(56.42 \pm 0.55) - (5.211 \pm 0.123)\} = 10^{-2}(51.21 \pm 0.56)$		
$w(\text{N})$ as Si ₃ N ₄ = $10^{-2} \{(37.70 \pm 1.09) - (3.891 \pm 0.014)\} = 10^{-2}(33.80 \pm 1.09)$		
$n(\text{Si})/n(\text{N}) = (0.7555 \pm 0.0257)^a$		

^acorresponds to Si₃N_{3.97±0.08}

Calorimetric experiments

Experiments showed that amorphous Si₃N₄ reacted spontaneously with fluorine and the reaction was not completed without the application of auxiliary combustant materials, which had to be used in the previous studies of crystalline α - and β -Si₃N₄ [6, 7]. As it was noted previously, the combustion of α -Si₃N₄ in fluorine proceeded according to



Because the reaction occurred spontaneously it was necessary to use a two-chamber bomb in order to isolate fluorine from the amorphous Si_3N_4 . The fluorine calorimetric laboratory at NIST and the outline of general experimental techniques were described in detail previously [9]. The calibration of this calorimetric system was performed by combustion of benzoic acid (NIST-SRM-39i) in oxygen and the energy equivalent was determined to be $\langle \epsilon(\text{calor}) \rangle = 13926.6 \pm 0.7 \text{ J K}^{-1}$ (the uncertainty is the standard deviation of the mean). Before the combustion of $a\text{-Si}_3\text{N}_4$ the bomb was preconditioned by performing a combustion of tungsten with small amount of sulphur in fluorine. All operations that exposed the interior of the bomb or the $a\text{-Si}_3\text{N}_4$ sample were performed in a glovebox. The sample was placed in the pre-fluorinated nickel crucible that rested on the lid of the reaction vessel. Pure fluorine at a pressure of $\cong 1 \text{ MPa}$ at $T \cong 293 \text{ K}$ (which corresponded to an amount of substance of F_2 of $\cong 0.1 \text{ mol}$) was confined to a tank that surrounded the reaction vessel and was connected to it via a remotely operable valve. After the tank and reaction vessel assembly has been placed in the calorimeter, the valve was opened and the combustion of $a\text{-Si}_3\text{N}_4$ started. The resulting temperature increase of the calorimeter was measured with a quartz-crystal thermometer. Afterwards, the products of fluorination were isolated and identified, and the reaction vessel was returned to the glovebox for examination. The inner surface of the bomb was examined and the crucible weighed, in a search for unreacted $a\text{-Si}_3\text{N}_4$ or other residual solids. Only after three experiments small residues of $a\text{-Si}_3\text{N}_4$ (of mass $< 0.8 \text{ mg}$) were found in crucible and removed by gentle brushing. The increase of mass of crucible during consecutive experiments was not observed thus the formation of NiF_2 was excluded in this case. The gaseous reaction products of selected experiments were condensed into a Monel trap immersed in a liquid nitrogen. After removal of excess F_2 by pumping, the remaining gases were analysed by FTIR. Only peaks attributable to SiF_4 were observed.

Results and discussion

Details of the calorimetric measurements on reaction (1) are given in Table 3. Eight consecutive experiments gave the individual results for the massic energy of combustion $\Delta_c u$ of $a\text{-Si}_3\text{N}_4$ samples. The values $\Delta_c u$ for each experiment were calculated by summing the contributing energy quantities in each vertical column of Table 3 and dividing by the corresponding $m(\text{Si}_3\text{N}_4)$ mass of the sample. For the conversion of apparent mass to mass m , the density of $a\text{-Si}_3\text{N}_4$ was taken to be 3.800 Mg m^{-3} . Calculations of the corrected temperature increase $\Delta\theta_c$, the correction for expansion of the fluorine and the gaseous combustion products $\Delta U(\text{gas})$, the correction for change of total energy content of the products and substrates of reaction $\Delta U(\text{cont})$, followed procedures recommended by Hubbard [10]. The correction for thermal effects associated with the use of two-compartment bomb $\Delta U(\text{blank}) = 5.71 \pm 1.05 \text{ J}$ was determined by running a series of blank experiments in which the amount of fluorine identical to that used in the reaction (1) was expanded into the empty combustion chamber. The

Table 3 Massic energy of combustion of α -Si₃N₄ in fluorine; $T=298.15$ K, $p^0=101.325$ kPa

	1	2	3	4	5	6	7	8
m/g	0.30697	0.23516	0.20712	0.17179	0.21521	0.22094	0.23671	0.25584
$\Delta\theta_c/K$	0.62661	0.48071	0.42363	0.35080	0.44038	0.45162	0.48391	0.52255
$\Delta U(\text{blank})/J$	5.71	5.71	5.71	5.71	5.71	5.71	5.71	5.71
$\Delta U(\text{gas})/J$	1.674	1.381	1.299	1.158	1.315	1.329	1.387	1.458
$\Delta U(\text{cont})/J$	-3.641	-2.767	-2.4437	-2.001	-2.531	-2.594	-2.779	-3.008
$\epsilon(\text{calor})(-\Delta\theta_c)/J^a$	-8726.55	-6694.66	-5899.73	-4885.45	-6132.99	-6289.53	-6739.22	-7277.34
$\Delta_c u/J g^{-1}$	-28415.8	-28450.13	-28462.50	-28410.17	-28476.84	-28447.03	-28452.13	-28428.64
$\langle \Delta_c u \{ \alpha\text{-Si}_3\text{N}_4 \} \rangle = -28443 \pm 7 J g^{-1b}$ impurity correction = $-677 \pm 43 J g^{-1c}$ $\Delta_c u^0 = -29120 \pm 88 J g^{-1d}$								

^aThe energy equivalent of the calorimetric system $\langle \epsilon(\text{calor}) \rangle = 13926.6 \pm 1.2 J K^{-1}$

^bThe massic energy of combustion calculated from the results of all experiments, uncertainty is the standard deviation of the mean of the individual values of $\Delta_c u$

^cUncertainty is the standard deviation of the mean; calculation outlined in Table 4

^dUncertainty corresponds to twice the standard deviation of the mean; calculation of uncertainty is outlined in text

Table 4 Detailed impurity corrections for α -Si₃N₄; w denotes mass fraction of impurity phase

Impurity phase	$w \cdot 10^2$	$\Delta_f H_m^0(\text{imp})^a/\text{kJ}$	$\Delta_c u(\text{imp})^b/\text{kJ g}^{-1}$	$\Delta(\Delta_c u)^c/\text{kJ g}^{-1}$	$w \cdot \Delta(\Delta_c u)^c/\text{J g}^{-1}$
SiC	0.419±0.021	-71.9	-61.57	33.13	139±7
SiO ₂	9.679±0.254	-901.4	-11.89	-16.55	-1602±42
NH ₃	0.0473±0.0005	-45.9	-45.06	16.62	780±8
Impurity correction/J g ⁻¹ :					-677±43

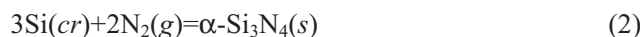
^aThe values of standard enthalpies of formation of impurity phases were taken from Gurvich *et al.* [5];

^bReactions of the impurity phases with fluorine are assumed to be following: SiC+4F₂=SiF₄+CF₄;

SiO₂+2F₂=SiF₄+O₂; NH₃+3/2F₂=3HF+1/2N₂. The massic energies of combustion of impurity phases with fluorine were calculated using the data of standard enthalpies of formation of impurity phases and fluorides taken from [5] and [14];

^c $\Delta(\Delta_c u)=\Delta_c u(\text{Si}_3\text{N}_4)-\Delta_c u(\text{imp})$; correction calculated on the basis of determined value of $\Delta_c u(\text{Si}_3\text{N}_4)= -28443 \pm 7 \text{ J g}^{-1}$ for α -Si₃N₄

procedure of determination and calculation of $\Delta U(\text{blank})$ was explained in detail by O'Hare [11]. Auxiliary quantities used in the calculation of standard state corrections were: C_p^0 of $\alpha\text{-Si}_3\text{N}_4$ ($0.78 \text{ J K}^{-1} \text{ g}^{-1}$); $C_{v,m}$ of F_2 , SiF_4 and N_2 respectively (22.99 , 65.31 and $20.81 \text{ J K}^{-1} \text{ mol}^{-1}$); second virial coefficients of F_2 , SiF_4 and N_2 (-19 , -139 and $5.1 \text{ cm}^3 \text{ mol}^{-1}$) taken from White *et al.* [12], Hamman *et al.* [13] and Heintz and Lichtenthaler [14]. Because the increase of the mass of crucible during the experiments was not observed, the use of correction for formation of NiF_2 was not necessary in this case. From the individual values of $\Delta_c u$ for each experiment the mean value of massic energy of combustion was calculated $-28443 \pm 7 \text{ J g}^{-1}$. This value combined with the impurity correction $-677 \pm 43 \text{ J g}^{-1}$ (calculation of which is outlined in Table 4) leads to the final result of standard massic energy of combustion $\Delta_c u^0 = -29120 \pm 88 \text{ J g}^{-1}$. The final uncertainties attached to the value of standard massic energy of combustion $\Delta_c u^0$ given as twice the standard deviation of the mean included the contributions from the experimental massic energies and impurity corrections and also the uncertainties from the following quantities $\Delta U(\text{blank})$, $\Delta U(\text{gas})$, $\Delta U(\text{cont})$ and $\varepsilon(\text{calor})(-\Delta\theta_c)$ combined together in quadrature. On the basis of the molar mass of silicon nitride $M(\text{Si}_3\text{N}_4) = 140.283 \text{ g mol}^{-1}$ and $\Delta_c u^0$ the molar energy of combustion $\Delta_c U_m^0 = -4085.0 \pm 12.0 \text{ kJ mol}^{-1}$ was derived. For reaction (1) the difference between the number of moles of gaseous products and substrates is $\Delta v^g = 3 + 2 - 6 = -1$ and with the constant $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$ the molar enthalpy of combustion $\Delta_c H_m^0 = -4087.5 \pm 12.0 \text{ kJ}$ of reaction (1) was calculated. The latter result, combined with $\Delta_f H_m^0(\text{SiF}_4, \text{g}, 298.15 \text{ K}) = -1615.8 \pm 0.5 \text{ kJ}$ [15] yields: $\Delta_f H_m^0(\alpha\text{-Si}_3\text{N}_4, \text{s}, 298.15 \text{ K}) = -760 \pm 12 \text{ kJ}$. Here, the uncertainties in the $\Delta_c H_m^0$ and $\Delta_f H_m^0(\alpha\text{-Si}_3\text{N}_4, \text{s}, 298.15 \text{ K})$ are combined in quadrature. The formation reaction is:



at $T = 298.15 \text{ K}$ and $p^0 = 101.325 \text{ kPa}$.

In Table 5 the thermodynamic properties of amorphous silicon nitride determined in this work are presented compared to the results obtained previously for α and β forms of crystalline Si_3N_4 [7]. The massic energy of combustion of $\alpha\text{-Si}_3\text{N}_4$ uncorrected for impurities (Table 3) is less negative than massic energies of combustion of crystalline α and β samples. However, when the impurity correction is applied, the massic energy of combustion of amorphous silicon nitride becomes more negative than the values determined for crystalline forms, leading in effect to less negative value of enthalpy of formation. Thus, the impurity correction has a predominant influence here on ranking of the three samples in order of their stability. High value of impurity correction and calculated uncertainties resulted mainly from the large amount of oxygen in the specimen. The assumption was made that all O impurity is ascribed to SiO_2 but it is possible that a small amount of oxygen can be dissolved within Si_3N_4 grains or present on the surface as $\text{Si}_2\text{N}_2\text{O}$ or nitride oxide [8]. Nevertheless, calculation of such impurity corrections is not possible at present because the indispensable thermochemical data are missing. The results compared in the last row of Table 5 are: $\Delta_f H_m^0 = -760 \pm 12 \text{ kJ}$ for amorphous Si_3N_4 , $\Delta_f H_m^0 = -828.9 \pm 3.4 \text{ kJ}$ for

α -Si₃N₄ and $\Delta_f H_m^0 = -827.8 \pm 2.5$ kJ for β -Si₃N₄. Thus, the enthalpies of formation correlate well with the expected trend of stabilities at $T=298.15$ K within the uncertainties of calorimetric measurements.

Table 5 Thermodynamic properties of silicon nitrides; $T=298.15$ K, $p^0=101.325$ kPa

	α -Si ₃ N ₄ ^a	α -Si ₃ N ₄ ^b	β -Si ₃ N ₄ ^b
$\Delta_c u^0 / \text{J g}^{-1}$	-29120±88	-28628±22	-28636±14
$\Delta_c U_m^0 / \text{kJ}$	-4085.0±12.0	-4016.0±3.1	-4017.1±2.0
$\Delta v^{\#} RT / \text{kJ}$	-2.5	-2.5	-2.5
$\Delta_c H_m^0 / \text{kJ}$	-4087.5±12.0	-4018.5±3.1	-4019.6±2.0
$\Delta_f H_m^0 / \text{kJ}$	-760±12	-828.9±3.4	-827.8±2.5

The results are based on fluorine combustions of: ^aamorphous silicone nitride prepared in Pulvermetallurgic Laboratory in Stuttgart Max Planck Institute by pyrolysis of polyvinylsilazane precursor VT50; ^bsingle phase α -nitride designated as UBE-ESP and β -Si₃N₄ prepared in Stuttgart from a material manufactured by Denka (Japan) [7]

Enthalpy of transition

Finally, the massic energies of combustion in Table 5 are combined to calculate the massic enthalpy change $\Delta_{\text{trs}} h^0 = -492 \pm 91$ J g⁻¹ for the transition:



Thus the molar enthalpy change determined for the first time for the transition from amorphous to α -crystalline form $\Delta_{\text{trs}} H^0 = 69 \pm 13$ kJ is evident, in spite of its large uncertainty.

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