

Crystallization Behaviour of Amorphous Silicon Nitride

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Abstract

The crystallization of amorphous polymer-derived Si_3N_4 was investigated. The transformation of the amorphous into the crystalline α -phase was determined to be diffusion-controlled. In this report, the rate constants and the activation energy as well as the temperature-dependent induction period τ of the crystallization reaction were calculated by using a modified Avrami–Erofe'ev equation.

Die Kristallisation von amorphem, aus Polysilazan hergestelltem Si_3N_4 wurde untersucht. Die Umwandlung der amorphen in die kristalline α -Phase konnte als diffusions-kontrollierte Reaktion bestimmt werden. In der vorliegenden Arbeit wurden die Geschwindigkeitskonstanten und die Aktivierungsenergie sowie die temperaturabhängige Induktionszeit τ der Kristallisationsreaktion über eine modifizierte Avrami–Erofe'ev-Gleichung berechnet.

On a étudié la cristallisation du Si_3N_4 amorphe obtenu à partir d'un polymère. On a établi que la transformation de la phase amorphe en phase cristalline α est contrôlée par diffusion. Les valeurs des constantes de vitesse, de l'énergie d'activation et de la période d'induction de la réaction de cristallisation fonction de la température (τ) ont été calculées à l'aide d'une équation Avrami–Erofe'ev modifiée.

Introduction

Silicon nitride has great potential as a high-temperature material in applications for engine

construction. In common, Si_3N_4 parts are produced powdermetallurgically by pressureless sintering or by hot or hot-isostatic pressing of appropriate powders in combination with sintering additives. The traditional methods for the manufacture of Si_3N_4 starting materials, namely, the nitridation of silicon and the carbonitridation of silica, are high-temperature syntheses ($T \geq 1673$ K) and yield crystalline powders. In contrast, the production of Si_3N_4 -based ceramics by pyrolysis of polysilazanes or via gas-phase reactions at temperatures as low as 1273 K results in the formation of amorphous materials.^{1,2} The crystallization of the amorphous phase is an additional reaction that has to be taken into account during the densification process (sintering) proceeding at higher temperatures up to the decomposition point of Si_3N_4 (2123 K at 0.1 MPa N_2). This transformation of the solid phase seems to be an interesting reaction in terms of its exothermal character increasing the energy difference between the amorphous starting powder and the polycrystalline sintered body, which may enhance the sintering activity. Furthermore, crystallization also occurs during subsequent heat-treatments of bulk-pyrolysed monoliths, such as amorphous Si_3N_4 fibres³ under application conditions. It is also useful to get more quantitative information on the crystallization behaviour of this material in order to support with kinetic data the observed particle-disintegration mechanism⁴ occurring during sintering of amorphous Si_3N_4 .

According to Ohdomari *et al.*,⁵ the structure of amorphous silicon nitride has been described by a continuous random network (CRN). The structural model constructed is in good agreement with

experimental results demonstrated by a comparison of the radial-distribution functions and the structure factors derived from the model with those from experimental data. Sawhill and Haggerty⁶ found a linear correlation between the specific surface area of a laser-induced chemical-vapour-deposited Si_3N_4 powder and the degree of crystallinity. Sintering experiments of the CVD- Si_3N_4 powder revealed that local densification and the formation of clusters occurred, which is postulated to be connected with the crystallization process. However, macroscopic densification was not observed. Sawhill⁷ found a nucleation-rate-controlled crystallization, and the value of the sum of the free energy of forming a critical nucleus ΔG_c and the activation energy for transport across the amorphous-crystalline interface Q could be determined to be 695 kJ/mole at 1600 K. Tsuge *et al.*⁸ reported on the crystallization of the grain-boundary glassy phase in the Si-Al-Y-N-O system and found a logarithmic dependence between the amount of amorphous phase and time.

The present work deals with the kinetics of the crystallization reaction of polymer-derived amorphous silicon nitride.

Experimental Procedures

Amorphous Si_3N_4 powder was produced by pyrolysis of a polyhydrochlorosilazane⁹ under flowing NH_3 atmosphere at 1273 K. The molecular composition of the polymeric starting material is given in Fig. 1. Pyrolysis was conducted in a quartz tube

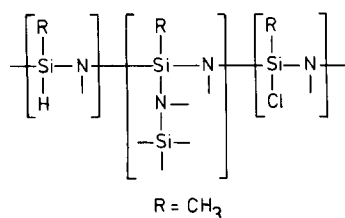


Fig. 1. Molecular composition of the polymeric hydrochlorosilazane (from Gerdau *et al.*⁹).

heated by a tube furnace. The as-produced colourless-powder agglomerates were milled in a porcelain mortar and passed through a 160- μm sieve. The sieved powder contained 33.3 wt% nitrogen, 5.3 wt% oxygen,[†] and 0.8 wt% residual chlorine as could be determined by chemical analysis. The oxygen contamination is due to the manipulation of the pyrolysed residue in air. Any carbon content was below the detectable limit. The heat treatment of the amorphous Si_3N_4 powders

[†] N and O Determinator Model TC 436, LECO Corporation, St. Joseph, Mississippi, USA.

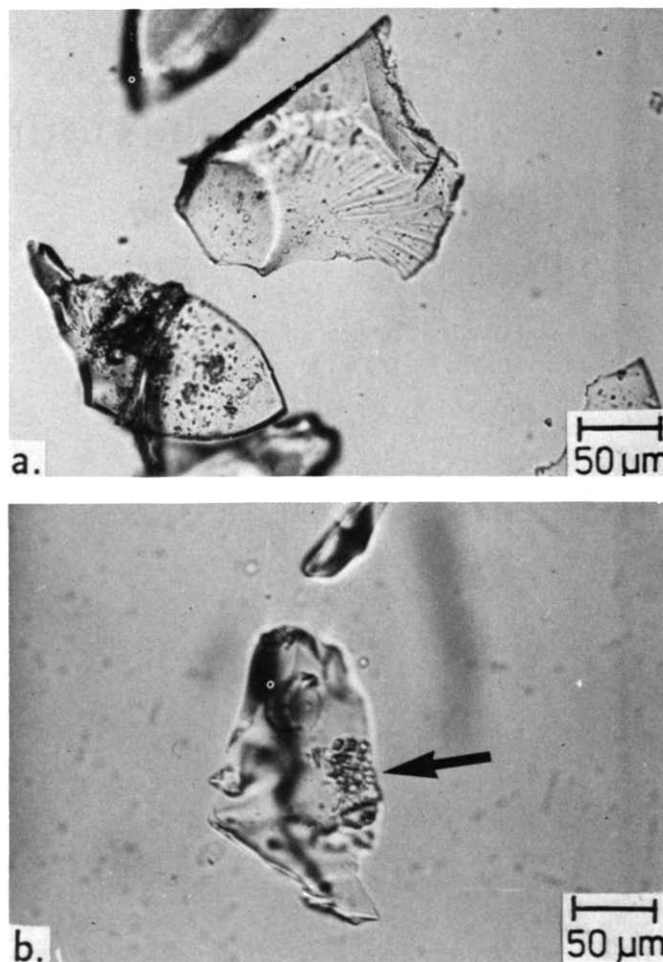


Fig. 2. Optical photomicrograph of (a) an amorphous (1000°C) and (b) a partly crystallized Si_3N_4 particle (1300°C). The crystallites are marked with an arrow.

was carried out in a resistively heated graphite furnace in N_2 atmosphere with a heating rate of 150 K/min. Qualitative phase analysis was undertaken by X-ray diffraction by using $\text{Cu}_{K\alpha}$ radiation ($\lambda = 154.18 \text{ pm}$). The crystallite sizes were determined by the line broadening of the (102) and (210) X-ray-diffraction lines by using the Scherrer equation.¹⁰ Quantitative phase analysis was undertaken by using the point-detection method with an optical transmission microscope at magnifications ranging from 50 to $400\times$. Figure 2 shows that amorphous and crystalline parts, even in the same particle, can be detected accurately. At each sample, 400 points were counted, leading to a statistical error of 5%. Isocrystalline curves in the time-temperature-transformation diagram (TTT diagram) given in Fig. 3 were calculated by linear interpolation between the determined values.

Results and Discussion

Crystallization of the polysilazane-derived amorphous Si_3N_4 started at temperatures above 1473 K. At

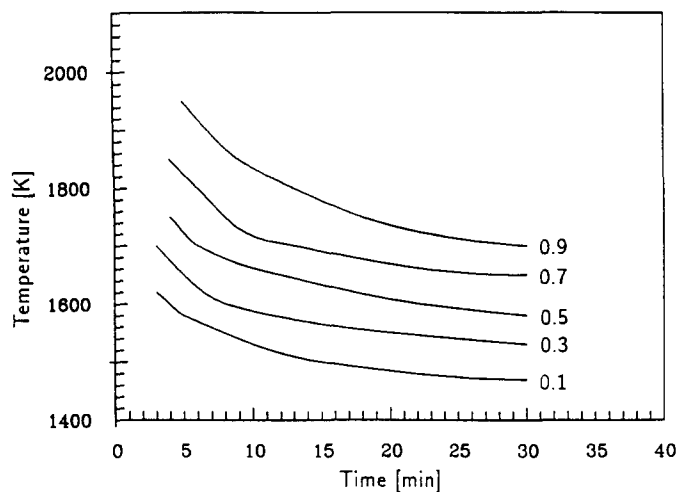
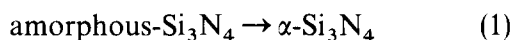


Fig. 3. Isothermal time-temperature-transformation (TTT) diagram of amorphous silicon nitride. The numbers in the diagram represent the degree of crystallinity.

this temperature, the degree of crystallinity was determined to be 10% at 30-min soaking time in N_2 atmosphere (Fig. 3). Qualitative phase analysis revealed that the crystallites shown in Fig. 2 consisted of α - Si_3N_4 , exclusively. The crystallite sizes ranged between 43 (1600 K) and 117 nm (1850 K) as can be seen from Table 1. From this, it is obvious that significant crystal growth occurred at temperatures exceeding 1750 K. Traces of β - Si_3N_4 could be detected only at high temperatures (2000 K) and long soaking times (30 min).

The isocrystalline curves in the TTT diagram in Fig. 3, as well as the isothermal curves in Fig. 4 representing the crystallization in terms of temperature vs time and amount of amorphous phase γ vs time, respectively, show close relations to the crystallization behaviour of glasses,¹¹ although the maximum temperature of the reaction



is limited by the decomposition temperature of Si_3N_4 at 2123 K and 0.1 MPa N_2 .¹²

We found that the decreasing relative amount of amorphous- Si_3N_4 denoted as γ with increasing time

Table 1. Kinetic data of crystallization of amorphous Si_3N_4 into the α -phase and crystallite size determined at various temperatures after a 15-min soaking time

Temperature T (K)	Rate constant k (1/s)	Induction period τ (min)	Crystallite size (nm)
1600	0.008	6.0	43
1650	0.019	4.9	—
1700	0.052	3.6	50
1750	0.089	2.4	57
1800	0.136	1.8	—
1850	0.186	1.1	117

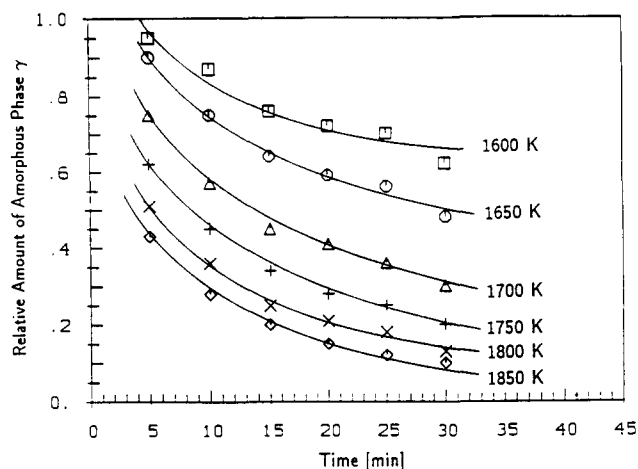


Fig. 4. Isothermal time-transformation diagram representing the decrease in the relative amount of amorphous Si_3N_4 denoted as a plot of γ against time.

at a given temperature (Fig. 4) can be satisfactorily described by the use of a modified Avrami-Erofe'ev equation (2):¹³

$$(-\ln \gamma)^{1/n} = k(t - \tau) \quad (2)$$

where n is the order of the equation, k the rate constant of the transformation, t the isothermal soaking time, and τ the induction period.

Generally, the induction period τ describes the delay in the crystallization, which is mainly due to a non-stationary period of nucleation.¹⁴ At $t \geq \tau$, the number of nuclei is proportional to the soaking time.¹⁵ Toschew¹⁶ calculated τ for supersaturated melts as a function of the surface tension σ , melting temperature T_s , molecular distance δ , viscosity η , heat of fusion Q_m , and undercooling ΔT according to eqn (3);

$$\tau = \frac{1.6 \cdot \sigma T_s^2 \delta^5 \eta}{Q_m^2 \Delta T^2} \quad (3)$$

In our calculation, τ should appear as a shift of the time axis in Fig. 4. It is assumed that no reaction obeying eqn (1) should occur between $t = 0$ and $t = \tau$. The experimental crystallization curves are then best fitted if the order n in eqn (2) is 0.5, i.e. if $(-\ln \gamma)^2$ is plotted against time as shown in Fig. 5. According to the literature,^{17,18} the value of $n = 0.5$ determined indicates that the rate-determining step of the solid-phase reaction represented by eqn (1) is diffusion rather than a chemical reaction.

The rate constants k can be calculated from the slopes of the curves given in Fig. 5 and τ from the axis intercept $k\tau$. The kinetic data determined are summarized in Table 1. The temperature-dependence of the rate constant k is given by the Arrhenius equation, eqn (4):

$$k = A_c \cdot \exp(-E_{ac}/R \cdot T) \quad (4)$$

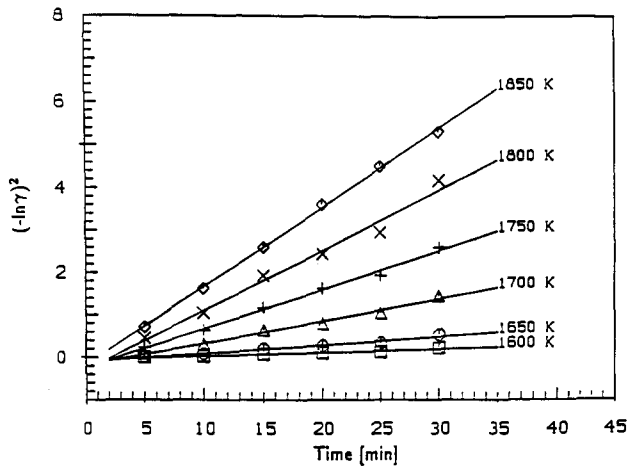


Fig. 5. Linear dependence of $(-\ln \gamma)^2$ on soaking time determined at various temperatures according to eqn (2).

where A_c is a frequency factor, E_{ac} the activation energy for crystallization, R the gas constant, and T the absolute temperature.

In order to calculate the activation energy of the crystallization reaction, namely, nucleation and crystal growth, the amounts of k evaluated were transformed into an Arrhenius plot (Fig. 6). From this, an activation energy of 306 kJ/mol is calculated for the reaction given in eqn (1). This value is in close agreement with the activation energies of crystallization observed for many oxidic materials.¹⁹

According to eqn (3), the induction period τ is directly proportional to the viscosity η . Hence the temperature-dependence of τ can be determined in a manner analogous to that of the viscosity by using eqn (5):¹¹

$$\tau = A_t \cdot \exp(E_{at}/R \cdot T) \quad (5)$$

where A_t is the frequency factor, E_{at} the activation energy for τ , and R and T have the usual meanings. From the plot of $\ln \tau$ against $1/T$ given in Fig. 7, E_{at} was evaluated to be 162 kJ/mol which is a relatively

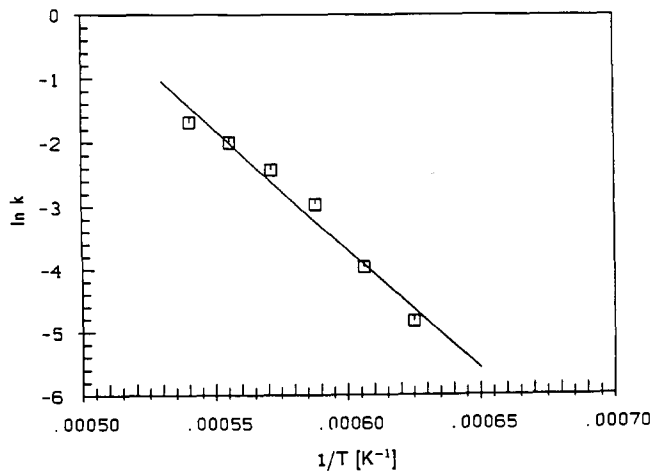


Fig. 6. Arrhenius plot of the rate constant $\ln k$ against $1/T$.

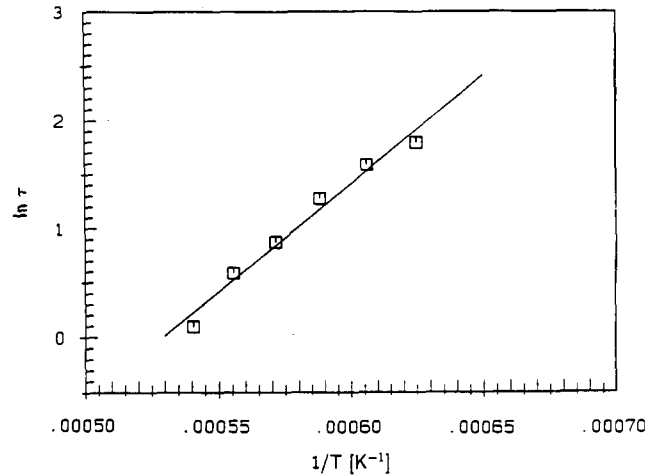


Fig. 7. Logarithmic representation of the induction period τ as a function of temperature in order to determine the activation energy of τ .

low amount in comparison with, for example, 440 kJ/mole determined for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass.¹¹ Thus the induction period of amorphous Si_3N_4 is far less temperature-dependent than that of the oxidic glass system ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$).

Conclusions

Crystallization of amorphous Si_3N_4 occurs at temperatures exceeding 1473 K to give α -silicon nitride. The crystallization is characterized by an activation energy of 306 kJ/mol and is diffusion-controlled. The isothermal crystallization process starts with a delay that is attributed to an induction period between 6 min at 1600 K and 1 min at 1850 K. The kinetic data determined show that the solid-phase transformation proceeds very rapidly at the common Si_3N_4 -sintering temperature (2123 K), so that the amorphous part will crystallize completely during pressureless densification or during subsequent heat-treatments of polysilazane-derived Si_3N_4 bulk materials (e.g. fibres). The amorphous phase may be sustained in part by applying lower sintering temperatures under hot or hot-isostatic pressing conditions. Thus the values can be exploited to adjust the degree of crystallinity during sintering or annealing of amorphous Si_3N_4 .

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