

Stresses Developed in Reaction-bonded Ceramics

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Abstract

A physical model is presented that predicts the stress distribution created in a particle during its reaction with a surrounding reactant to form a uniform layer of reaction product on its surface, when the reaction involves a volume change. The results of the model are applied specifically to the case of silicon reacting with nitrogen to form Si_3N_4 . The model predicts the generation of a high, tensile hydrostatic stress in the Si core as well as high tensile radial stress and compressive tangential stress in the nitride layer. Although the model is restricted to elastic deformation only and therefore predicts unrealistically high stresses in some cases, the results are anyway of relevance in the consideration of possible non-elastic processes such as creep and fracture and also in assessing the possible effect of stress on the reaction equilibrium. It is predicted that the nitride reaction layer would fracture during the nitridation process. A second model is also presented predicting the residual stresses arising during cooling of a partially reacted particle as a result of the difference in thermal expansion of the reactant core and the reaction product layer. In the case of the reaction of silicon to silicon nitride these thermal expansion mismatch stresses are significant but small compared to the stresses due to the chemical reaction. © 1999 Elsevier Science Limited. All rights reserved

Keywords: Si_3N_4 , reaction bonding, stress development, modelling.

1 Introduction

The present work concerns the mechanical stresses at a microstructural level that can be generated during the reaction of solid particles of reactant A with an external reactant B such that the volume of

the reaction product is greater than that of A. A typical example of such a reaction would be the reaction of solid particles with a gas to form a solid reaction product. The phenomena concerned are of a general nature but here the treatment will be exemplified specifically by the reaction of silicon powder with nitrogen gas to form silicon nitride. This reaction is of practical interest since it is the basis of the production of so-called reaction bonded silicon nitride (RBSN) a structural ceramic. Moreover, this process has been the subject of considerable study over a number of decades.^{1–5} The reaction itself involves an increase in volume of around 22%. However, a characteristic of the RBSN process is that during the nitridation of compacted silicon powder, the external dimensions of the compact do not change significantly, i.e. the increase in volume due to the reaction is accommodated internally. This is not necessarily unreasonable since such a compact typically contains 40–50% porosity prior to the reaction; however, any model of the process must be consistent with this observation.

Many possible mechanisms can be proposed for this type of reaction. The simplest models assume a spherical particle reacting to form a uniform layer of reaction product on the surface. The resulting kinetics and morphological development of the compact then depend on the kinetics of the transport of the reactants through the reaction layer, namely, of the gas inwards and the solid outwards. The relative importance of the various transport paths in the case of the RBSN process is still unclear but they are presumably sensitive to a number of the process variables. Whatever the details of the reaction, it can be assumed that if the solid reactant and reaction product maintain a bonded interface with each other, internal stresses must be generated around the interface as a result of the volume change.

In the present work the stresses are considered that are generated in a particle for which the reaction

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occurs by diffusion of the reactant gas through the reaction layer to the solid react core, the so-called shrinking core model. For silicon nitride, this corresponds to nitrogen diffusing through a layer of silicon nitride to react at the nitride layer/silicon core interface. In earlier studies it has been recognised that such a process would lead to high compressive stresses in the nitride layer. These could subsequently be sufficient to cause rupture of the layer resulting in a flake-like reaction product and a consequent modification of the reactant transport kinetics.^{1,4,5} It has been argued that the shrinking core model is not possible in the nitridation of silicon since it would necessitate a space creating mechanism at the interface.³ However, such a space creating process might be possible if tensile stresses were to be generated at the interface.

To further explore and develop such ideas and models it is necessary to have a more accurate, quantitative knowledge of the stress and strain distribution associated with the reaction. Therefore, in this work a physically-based mathematical model is developed to predict the stresses and strain generated in a reacting, spherical particle and this is illustrated by the reaction of silicon and nitrogen to form silicon nitride. The model is restricted to elastic deformation, i.e. it predicts stresses without taking into account stress-relieving processes such as plasticity, creep or fracture. However the predicted stresses are of relevance and can be applied when considering the possible occurrence of such non-elastic processes and this is illustrated here for the case of brittle fracture of the reaction layer.

A second source of residual stress in a partially-reacted compact is the possible difference in thermal expansion between that of the reactant and reaction product. This thermal expansion mismatch leads to the creation of an internal stress state if the temperature changes, a stress state that would superimpose on that created by the reaction. Expressions are derived here for such a mismatch stress state and again these are illustrated by the RBSN system.

2 Formulation of Stresses During Nitridation

2.1 Physical description

According to the 'sharp interface' and 'core shrinkage' models,²⁻⁵ the solid-gas reaction starts from the surface of a particle, forming a shell of reaction product which then grows inwards. In the RBSN process, each particle consists initially of a silicon core surrounded by a Si_3N_4 layer. It is assumed that the reaction progresses inwards by

nitrogen diffusion through the previously formed nitride shell, forming new product at the $\text{Si}/\text{Si}_3\text{N}_4$ interface. Consequently, stresses will develop within the Si_3N_4 shell and the Si core due to the volumetric increase when Si is converted to Si_3N_4 .

If the compact is cooled before the reaction is complete, i.e. silicon cores remain in the particles, thermal expansion mismatch between the two materials will result in thermal stress during cooling from the reaction temperature. The thermal stress superimposed on the stress due to the volumetric expansion will remain after the reaction process.

For mathematical simplification, it is assumed that the particles in the reacting powders are single sized spheres and the force acting on a particle due to its neighbours is neglected. The latter assumption means that a particle is isolated from the powder compact and the stresses and strains within the particle are analysed. In practice, during nitridation, each particle changes its shape and area of contact with its neighbours while the coordination number (the number of contacts per particle) increases. A powder compact can then be visualised as made of Voronoi polyhedra⁶ and the truncated particle can be assumed to be approximated by a sphere of equivalent volume in the mathematical treatment of the model.

2.2 Mathematical formulation

Consider a silicon particle isolated from a powder compact with the initial radius R_{SO} (see Fig. 1). It is imagined that for an arbitrary stage of the reaction the particle is separated into a silicon core, A , of radius R_C and a silicon shell, B , corresponding to the material that is reacted, (outer-radius R_{SO} and inner-radius R_C). When the silicon shell, B , is transformed to Si_3N_4 , B' , by the nitriding reaction: $3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$, the volume alters and the outer and inner radius become $R_{\text{SO}}(1 + \alpha)$ and $R_C(1 + \alpha)$, respectively, where α is the linear expansion coefficient due to the volume change.

The final state of the partially-reacted particle is obtained by re-uniting the core and shell, AB' . To

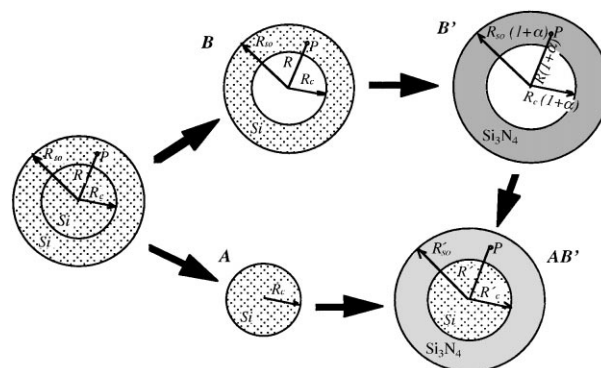


Fig. 1. Schematic diagram showing how to construct the model.

achieve this, since the dimensions of the Si_3N_4 shell, B' , and the silicon core, A , are no longer compatible, the Si_3N_4 shell must be constrained and the Si core stretched, so that R , R_{SO} and R_C become R' , R'_{SO} and R'_C , respectively. This imaginary operation can be used as the basis for deriving the strains and stresses arising from the partial reaction.

On the basis of the spherical symmetry, a general expression for stresses and displacement is given by elasticity theory⁷ as:
for the silicon core:

$$\left. \begin{aligned} u_A &= C_{1A} \times r + \frac{C_{2A}}{r^2} \\ \sigma_{r,A} &= C_{1A} \times P - \frac{C_{2A}Q}{r^3} \\ \sigma_{t,A} &= C_{1A} \times P + \frac{C_{2A}Q}{2r^3} \end{aligned} \right\} \quad (1)$$

and for the Si_3N_4 shell,

$$\left. \begin{aligned} u_{B'} &= C_{1B'} \times r + \frac{C_{2B'}}{r^2} \\ \sigma_{r,B'} &= C_{1B'} \times M - \frac{C_{2B'}N}{r^3} \\ \sigma_{t,B'} &= C_{1B'} \times M + \frac{C_{2B'}N}{2r^3} \end{aligned} \right\} \quad (2)$$

where

$$\left. \begin{aligned} M &= \frac{E_{\text{SN}}}{1-2\nu_{\text{SN}}} & N &= \frac{2E_{\text{SN}}}{1+\nu_{\text{SN}}} \\ P &= \frac{E_S}{1-2\nu_S} & Q &= \frac{2E_S}{1+\nu_S} \end{aligned} \right\} \quad (3)$$

and u is displacement, σ_r radial stress, σ_t tangential stress, E elastic modulus, ν Poisson's ratio, r radial coordinate and the subscripts A , B' , S and SN denote the core, A , the shell, B' , silicon and Si_3N_4 , respectively. C_1 and C_2 in eqn (1) and (2) are constants which can be determined from the boundary conditions of the operation of joining A to B' , namely: (1) the radial stresses in A and B' at their interface are equal; (2) the radial stress at the outer surface of B' is zero; (3) the displacement at the centre of the Si core, A , is zero; (4) the algebraic sum of the displacements of A and B' at the interface equals the difference between the inner radius of B' and outer radius of A .

With these boundary conditions eqn (1) and (2) yield:

$$\left. \begin{aligned} PC_{1A} - \frac{QC_{2A}}{R_C^3} - MC_{1B'} + \frac{NC_{2B'}}{[R_C(1+\alpha)]^3} &= 0 \\ MC_{1B'} - \frac{NC_{2B'}}{[R_{\text{SO}}(1+\alpha)]^3} &= 0 \\ C_{1A} \times 0 + \frac{C_{2A}}{0^2} &= 0 \\ R_C C_{1A} + \frac{C_{2A}}{R_C^2} - R_C(1+\alpha)C_{1B'} - \frac{C_{2B'}}{[R_C(1+\alpha)]^2} &= R_C\alpha \end{aligned} \right\} \quad (4)$$

Solving eqn (4) gives,

$$C_{1A} = \frac{1}{\Delta_1} \begin{vmatrix} 0 & -M & N/[R_C(1+\alpha)]^3 \\ 0 & M & -N/[R_{\text{SO}}(1+\alpha)]^3 \\ R_C\alpha & -R_C(1+\alpha) & -1/[R_C(1+\alpha)]^2 \end{vmatrix} \quad (5)$$

$$C_{1B'} = \frac{1}{\Delta_1} \begin{vmatrix} P & 0 & N/[R_C(1+\alpha)]^3 \\ 0 & 0 & -N/[R_{\text{SO}}(1+\alpha)]^3 \\ R_C & R_C\alpha & -1/[R_C(1+\alpha)]^2 \end{vmatrix} \quad (6)$$

$$C_{2B'} = \frac{1}{\Delta_1} \begin{vmatrix} P & -M & 0 \\ 0 & M & 0 \\ R_C & -R_C(1+\alpha) & R_C\alpha \end{vmatrix} \quad (7)$$

$$C_{2A} = 0 \quad (8)$$

In eqns (5)–(7)

$$\Delta_1 = \begin{vmatrix} P & -M & N/[R_C(1+\alpha)]^3 \\ 0 & M & -N/[R_{\text{SO}}(1+\alpha)]^3 \\ R_C & -R_C(1+\alpha) & -1/[R_C(1+\alpha)]^2 \end{vmatrix} \quad (9)$$

The stress distribution as a function of the radial distance from the particle centre, R , and the radius of the silicon core, R_C , can be calculated by combining eqns (1)–(9). Since C_{2A} is equal to zero, stresses in the silicon core are hydrostatic, i.e.

$$\sigma_r(\text{in silicon}) = \sigma_t(\text{in silicon}) = C_{1A}P \quad (10)$$

For a given reaction $C_{(\text{solid})} + D_{(\text{gas})} \rightarrow CD_{(\text{solid})}$, providing the shrinking core mechanism is applied and the volume expansion ratio is α_{CD} , the stresses in the solid reactant core, $\sigma_{r,C}$, the radial and tangential stress in the product layer, $\sigma_{r,CD}$, $\sigma_{t,CD}$, can be expressed as (Appendix A):

$$\left. \begin{aligned} \sigma_{r,C} &= \sigma_{t,C} = \alpha_{\text{CD}} \times (1-k^3)f(\alpha_{\text{CD}}, k, E, \nu) \\ \sigma_{r,CD} &= \alpha_{\text{CD}} \left[1 - (1+\alpha_{\text{CD}})^3 (R_{\text{SO}}/r)^3 \right] f(\alpha_{\text{CD}}, k, E, \nu) \\ \sigma_{t,CD} &= \alpha_{\text{CD}} \left[1 + \frac{(1+\alpha_{\text{CD}})^3}{2} \left(\frac{R_{\text{SO}}}{r} \right)^3 \right] f(\alpha_{\text{CD}}, k, E, \nu) \end{aligned} \right\} \quad (11)$$

where $k = \frac{R_{\text{SO}}}{R_C}$ and $f(\alpha_{\text{CD}}, k, E, \nu) = \left[\frac{(1-k^3)}{P} - (1+\alpha_{\text{CD}}) \left(\frac{k^3}{N} + \frac{1}{M} \right) \right]^{-1}$. The subscripts c and CD denote reactant C and product CD, respectively. For a given reaction system, Young's modulus, E , Poisson's ratio, ν , volume expansion ratio, α_{CD} , are known constants and $f(\alpha_{\text{CD}}, k, E, \nu)$

is only a function of the reaction fraction, $\frac{\Delta V}{V}$. The stresses in materials of the reaction system can then be calculated by using eqn (11).

3 Thermal and Residual Stresses

If the reaction process is interrupted before completion and the system is cooled, then residual stresses will develop in both the core and reaction product layer as a result of thermal expansion mismatch between the two phases. It can be shown (Appendix B) that these stresses are given by:

$$\left. \begin{aligned} \sigma_{r,SN}^{th} &= \frac{2}{3} \frac{\alpha_{SN} E_{SN} T}{1-\nu_{SN}} \left(\frac{r^3 - R_C^3}{r^3} \right) + MC_{1H} + \frac{N}{r^3} C_{2H} \\ \sigma_{t,SN}^{th} &= -\frac{1}{3} \frac{\alpha_{SN} E_{SN} T}{1-\nu_{SN}} \left(\frac{r^3 - R_C^3}{r^3} \right) + MC_{1H} + \frac{N}{2r^3} C_{2H} - \frac{\alpha_{SN} E_{SN} T}{1-\nu_{SN}} \\ \sigma_{r,S}^{th} &= \sigma_{t,S}^{th} = \frac{2}{3} \frac{\alpha_S E_S T}{1-\nu_S} + PC_{1I} \end{aligned} \right\} \quad (12)$$

where superscript *th* denotes the thermal stress, α_{SN} and α_S are the thermal expansion coefficients of Si_3N_4 and Si, respectively, T the reaction temperature and r the radial coordinate. C_{1H} , C_{2H} and C_{1I} , are given in Appendix B. R'_{SO} and R'_C are the outer and inner radius, respectively, of the shell before cooling, calculated using equations given in Appendix B.

4 Results and Discussion

4.1 Predicted stress distribution

It is of interest to know the local distribution of stresses in both phases at any arbitrary stage of the reaction as well as how the stress state evolves as the reaction proceeds. Here the results are presented as a function of both R/R_{SO} , which represents the relative radial distance from the centre of the particle and R_C/R_{SO} representing the degree of reaction (i.e. the relative radius of remaining unreacted core). Results for the reaction of silicon to silicon nitride (based on the elastic properties given in Appendix C) are summarised in Figs 2 and 3 which show the tangential and radial stress distributions through the particle, respectively. The results are shown for increasing degrees of reaction (decreasing R_C/R_{SO}). The tangential stress in the silicon core is omitted from Fig. 2 since this is constant through the core and equal to the radial stress (i.e. the stress in the core is hydrostatic).

The following conclusions can be drawn from the results:

- The radial stresses in the silicon core and nitride layer are both tensile throughout the reaction process.

- The tangential stresses are tensile in the core but compressive in the nitride layer throughout the process.
- The stress in the core is hydrostatic and *tensile* throughout the process. This result is perhaps counter-intuitive. It has implications for the RBSN process since it dispels the suggestion that the reaction might be inhibited by a compressive stress in the core.
- The compressive tangential stress in the nitride layer is greatest at the start of the reaction process and decreases progressively with the degree of reaction.
- The tensile radial stress in the nitride layer is maximum at the layer/core interface where it equals the core stress. This stress increases with the degree of reaction, approaching a limiting value (see Fig. 4).
- The stress level for a given degree of reaction and for a given set of elastic constants exhibit approximately linear dependence upon the volume expansion ratio of the reaction product. This is illustrated in Fig. 5 for the core

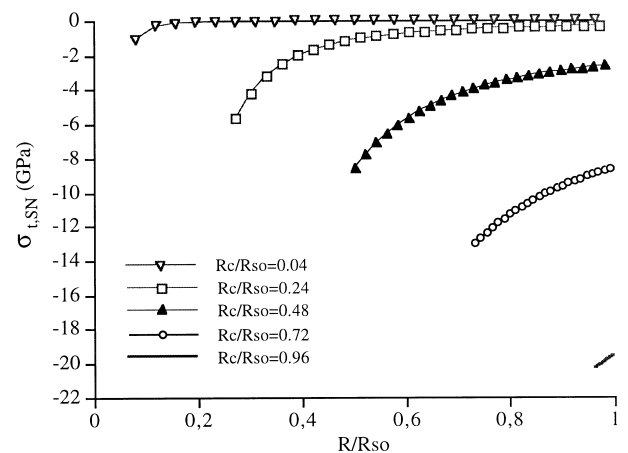


Fig. 2. Distribution of the tangential stress within the Si_3N_4 layer at 1400°C .

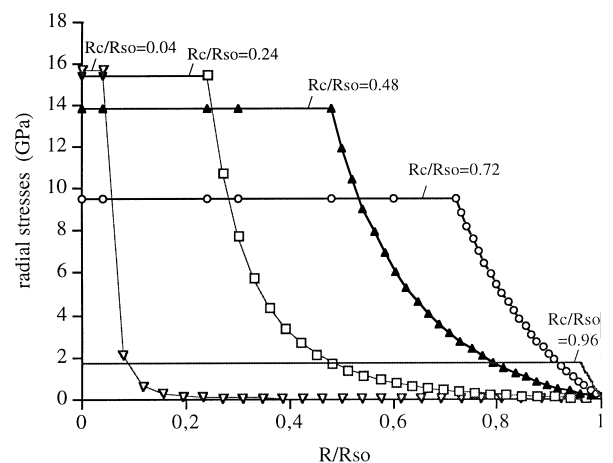


Fig. 3. Distribution of the radial stress in the particle at 1400°C .

stress assuming elastic properties equal to those of silicon and silicon nitride given in Appendix C.

4.2 Some implications of the results

The above model is based on the maintenance of the spherical core/shell geometry and is restricted to elastic strains only. Consequently, extremely high stresses are predicted locally during the reaction process. In reality, these would almost certainly lead to non-elastic deformation processes such as creep and fracture with a consequent partial relaxation of the stresses and deviation from the model. However, the model provides a valuable guide to the nature of such processes. For example, the high tensile stress in the silicon core, since it is hydrostatic would be unlikely to lead to fracture but could well lead to cavity formation through vacancy condensation followed by silicon vapourisation. Cavity formation in the silicon phase is indeed a common observation in the RBSN process.

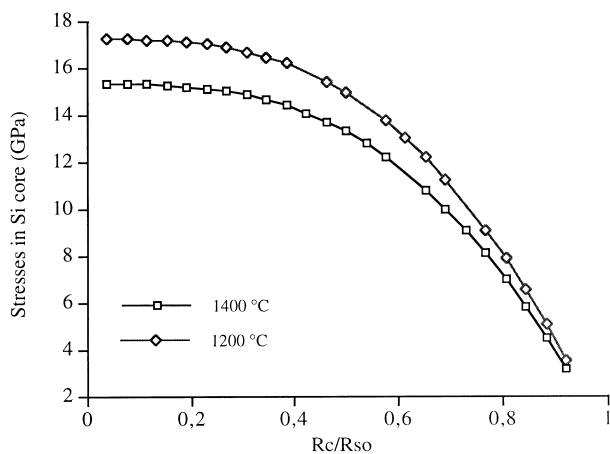


Fig. 4. Variation of the hydrostatic stress within Si core (and maximum radial stress in the nitride layer) versus R_C/R_{SO} at 1200 and 1400 °C. The higher level at 1200 °C arises from the higher values of the elastic moduli.

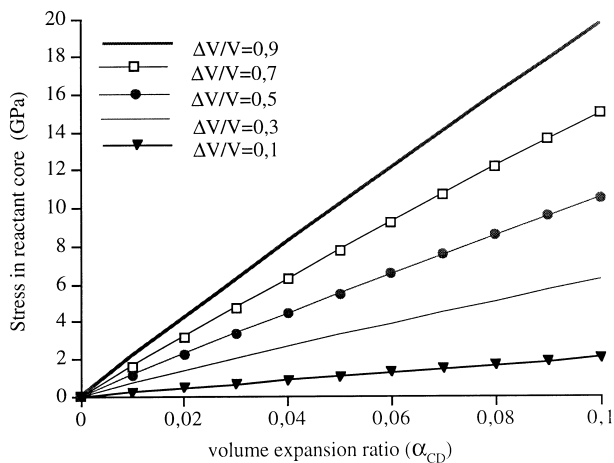


Fig. 5. Stress in the reactant core versus the volume expansion ratio of reaction product (α_{CD}) and the volume fraction of reaction ($\Delta V/V$).

It can also be seen that conditions for space creation at the reaction front as stipulated by Jennings³ do indeed exist.

The stresses generated in the nitride layer are sufficient to give fracture. However, the details of crack initiation and subsequent failure process are difficult to predict. Initiation is expected to be difficult since dislocation activity is low and diffusion slow in silicon nitride because of its highly covalent character. A possible source of crack initiation could be for example growth defects. A feasible sequence of failure is that a defect lying normal to the tensile radial stress becomes critical and leading to the growth of a circumferential crack and a simultaneous shear failure across the layer which would result in spalling of the layer. If for example it is assumed that the fracture toughness, K_c , of the nitride lies between 2 and 5 MPa \sqrt{m} (the value will depend on the crystallographic orientation) and applying the relation for fracture stress $\sigma = K_c/\sqrt{\pi a}$ a defect size of 0.1 μm would lead to a failure stress in the range 3–10 GPa. According to the present model, this range of radial stress in the layer corresponds to R_C/R_{SO} values in the range of 0.9 to 0.7. On a 2 μm diameter particle this corresponds to spallation thicknesses of around 100–300 nm, the same order of magnitude as observed experimentally by Kioke and Kimura.⁸

4.3 Thermal expansion mismatch stresses

The radial residual thermal expansion mismatch stress in the nitride layer calculated according to eqn (12) using the property data given in Appendix C is summarised in Fig. 6 where it is given as a function of R/R_{SO} and R_C/R_{SO} . It can be seen that the stress increases from the outer surface inwards and rises sharply to a maximum at the layer/core interface. The stress level increases as the reaction proceeds. The stress level is small relative to the stresses generated by the nitriding reaction. However

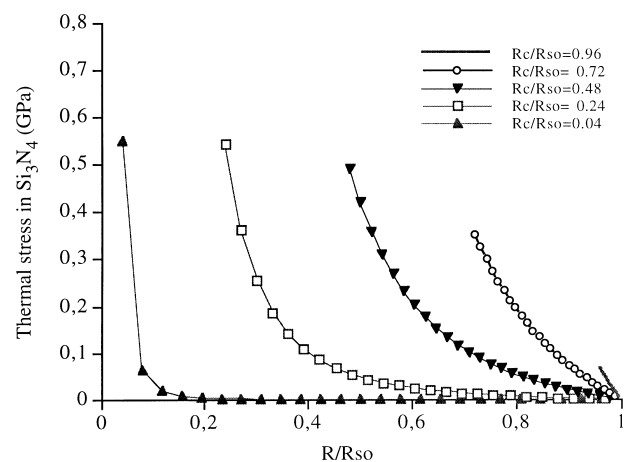


Fig. 6. Radial thermal stresses in Si_3N_4 after cooling from 1200 °C.

in absolute terms the level is not insignificant and should be considered in the general case, for example in systems in which the stresses due to the reaction are less important.

5 Conclusions

1. Mathematical models have been presented that predict (a) the instantaneous stresses in a particle during a reaction process in which a layer of reaction product is formed with a change in volume, (b) the residual stresses generated in the partially reacted particle during cooling after the reaction as a result of differences in the thermal expansion coefficients of the two phases (reactant and product).
2. The models have been applied to the specific case of the reaction of silicon with nitrogen to form silicon nitride. In the silicon nitride reaction layer the tangential stress is compressive while the radial stress is tensile; both increase from the outer surface towards the nitride/silicon interface. The stress in the silicon core is hydrostatic and tensile. As the nitriding reaction proceeds the level of tangential stress in the nitride layer decreases while the stress in the silicon core and the maximum radial stress in the nitride close to the interface increase.
3. The stress levels predicted are locally extremely high and are expected to lead to creep and fracture processes.
4. In the nitriding of silicon the stresses generated by thermal expansion mismatch during cooling are predicted to reach levels around 500 MPa and are small compared to those generated by the chemical reaction. However, such stress levels are significant in the general case.

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Appendix A

Stress equations for a given reaction

Putting eqns (3), (5), (8) and (9) into (1) yields:

$$\sigma_{r,A} = \alpha \times (1 - k^3) f(\alpha, k, E, \nu) \quad (\text{A1})$$

and

$$\sigma_{t,A} = \sigma_{r,A} \quad (\text{A2})$$

where $k = \frac{R_{SO}}{R_C}$ and $f(\alpha, k, E, \nu) = \left[\frac{(1-k^3)}{P} - (1 + \alpha) \left(\frac{k^3}{N} + \frac{1}{M} \right) \right]^{-1}$.

Putting eqns (3), (6), (7) and (9) into (2) yields:

$$\left. \begin{aligned} \sigma_{r,B'} &= \alpha \left[1 - (1 + \alpha)^3 (R_{SO}/r)^3 \right] f(\alpha, k, E, \nu) \\ \sigma_{t,B'} &= \alpha \left[1 + \frac{(1+\alpha)^3}{2} \left(\frac{R_{SO}}{r} \right)^3 \right] f(\alpha, k, E, \nu) \end{aligned} \right\} \quad (\text{A3})$$

For a given reaction $C_{(\text{solid})} + D_{(\text{gas})} \rightarrow CD_{(\text{solid})}$, providing the shrinking core mechanism is applied and the volume expansion ratio is α_{CD} , the stresses in the solid reactant core, $\sigma_{r,C}$, the radial and tangential stress in the product layer, $\sigma_{r,CD}$, $\sigma_{t,CD}$, can be expressed as:

$$\left. \begin{aligned} \sigma_{r,C} &= \sigma_{t,C} = \alpha_{CD} \times (1 - k^3) f(\alpha_{CD}, k, E, \nu) \\ \sigma_{r,CD'} &= \alpha_{CD} \left[1 - (1 + \alpha_{CD})^3 (R_{SO}/r)^3 \right] f(\alpha_{CD}, k, E, \nu) \\ \sigma_{t,CD'} &= \alpha_{CD} \left[1 + \frac{(1+\alpha_{CD})^3}{2} \left(\frac{R_{SO}}{r} \right)^3 \right] f(\alpha_{CD}, k, E, \nu) \end{aligned} \right\} \quad (\text{A4})$$

where $f(\alpha_{CD}, k, E, \nu) = \left[\frac{(1-k^3)}{P} - (1 + \alpha_{CD}) \left(\frac{k^3}{N} + \frac{1}{M} \right) \right]^{-1}$. The subscripts C and CD denote reactant C and product CD, respectively.

Since the reaction fraction, $\frac{\Delta V}{V} = 1 - \left(\frac{R_C}{R_{SO}} \right)^3$, for a given reaction system the Young's modulus, E ,

Poisson's ratio, ν , and α_{CD} are known constants. Therefore $f(\alpha_{CD}, k, E, \nu)$ is only a function of volume fraction of the reaction.

Appendix B

Equations for thermal stresses

The particle before cooling consists of a Si_3N_4 shell (with the inner radius R'_C and the outer radius R'_{SO}) and a silicon core of radius R'_C (Fig. 1). From the displacement u_A and u_B , in eqns (1) and (2), R'_C and R'_{SO} can be expressed as:

$$\left. \begin{aligned} R'_C &= R_C(1 + C_{1A}) \\ R'_{SO} &= R_{SO}(1 + \alpha) \left\{ 1 + C_{1B'} + \frac{C_{2B'}}{[R_{SO}(1 + \alpha)]^3} \right\} \end{aligned} \right\} \quad (\text{B1})$$

The thermal displacement (U^{th}) and stresses in the nitride shell and the silicon core after cooling can be expressed by⁷:

$$\left. \begin{aligned} U_{SN}^{th} &= -\frac{(1 + \nu_{SN})\alpha_{SN}T}{3(1 - \nu_{SN})} \frac{(r^3 - R_C^3)}{r^2} + C_{1H}r + \frac{C_{2H}}{r^2} \\ \sigma_{r,SN}^{th} &= \frac{2\alpha_{SN}E_{SN}T}{3(1 - \nu_{SN})} \frac{(r^3 - R_C^3)}{r^3} + MC_{1H} - \frac{NC_{2H}}{r^3} \\ \sigma_{t,SN}^{th} &= -\frac{\alpha_{SN}E_{SN}T}{3(1 - \nu_{SN})} \frac{(r^3 - R_C^3)}{r^3} + MC_{1H} + \frac{NC_{2H}}{2r^3} - \frac{\alpha_{SN}E_{SN}T}{(1 - \nu_{SN})} \\ U_S^{th} &= -\frac{(1 + \nu_S)\alpha_S T}{3(1 - \nu_S)} \times r + C_{1I}r + \frac{C_{2I}}{r^2} \\ \sigma_{r,S}^{th} &= \frac{2\alpha_S E_S T}{3(1 - \nu_S)} + PC_{1I} - \frac{QC_{2I}}{r^3} \\ \sigma_{t,S}^{th} &= -\frac{\alpha_S E_S T}{3(1 - \nu_S)} + PC_{1I} + \frac{QC_{2I}}{2r^3} - \frac{\alpha_S E_S T}{(1 - \nu_S)} \end{aligned} \right\} \quad (\text{B2})$$

where M, N, P and Q are material constants defined by eqn (3), C_{1H}, C_{2H}, C_{1I} and C_{2I} are constants determined by conditions given below.

1. The radial stresses of the shell and the core are equal at their interface, i.e.

$$\sigma_{r,SN}^{th}(R'_C) = \sigma_{r,S}^{th}(R'_C)$$

2. The radial stress of the shell at its outer surface is zero, i.e.

$$\sigma_{r,SN}^{th}(R'_{SO}) = 0$$

3. The displacement of the core at its centre equals zero, i.e. $U_S^{th}(0) = 0$
4. The displacement of the two parts is equal at the interface, i.e.

$$U_{SN}^{th}(R'_C) = U_S^{th}(R'_C)$$

Combining eqns (B1) and (B2) under the boundary conditions yields four equations containing C_{1H}, C_{2H}, C_{1I} and C_{2I} as unknown variables. Solving these four equations leads to four expressions for C_{1H}, C_{2H}, C_{1I} and C_{2I} ($=0$). Substituting these expressions back to eqn (B1), the thermal stresses can be calculated as given by eqn (12) in the text.

Appendix C

Data used in calculations

Table A1.

Parameter	(Conditions, Units)	Value	Reference
E_S	(1200 °C, GPa)	99.65	9
E_S	(1400 °C, GPa)	88.7	9
α		0.07	
α_S	(10 ⁻⁶ /°C)	5	10
ν_S		0.42	9
ν_{SN}		0.25	11
E_{SN}	(1200 °C, GPa)	282	12
E_{SN}	(1400 °C, GPa)	251	12
α_{SN}	(10 ⁻⁶ /°C)	3	10

Thermoelastic properties of silicon and of silicon nitride as used in the stress calculations (the references relate to the listing for the main paper).