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α–β phase transformation of silicon nitride – computer simulation

P. ŠAJGALÍK*
Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, CS-842 36 Bratislava, Czechoslovakia

The simulation model of α–β silicon nitride phase transformation was developed for the case when the crystallization of the β phase is the rate controlling step. The results gained on the base of the present model indicate that the temperature and total free surface area of β silicon nitride phase present in the "firing" body limit the rate of transformation and total amount of transformed β silicon nitride phase. These results are acceptable from the point of view of experimental experience and support the applicability of the presented model.

1. Introduction

The α–β silicon nitride phase transformation has been intensively studied [1–8] because of the toughening effect of the needle-like β silicon nitride grains in the resulting microstructure of the sintered body. Up to now, the problem of stability of the α and β silicon nitride phases has not been completely understood. Generally, it is accepted that the β silicon nitride phase at higher temperatures is more stable than the α silicon nitride phase. The oxide additives, such as Al_2O_3, Y_2O_3, MgO, and Nd_2O_3, enhance the rate of α–β silicon nitride phase transformation during the sintering. The kinetics of this process has been investigated with respect to the sintering temperature, chemistry of additive, morphology of silicon nitride powder and starting content of β silicon nitride phase [1–8]. Knowledge about the influence of these factors on the phase transformation kinetics serves as the basis for estimation of the mechanisms of the α–β silicon nitride phase transformation. Two basic phase transformation rate limiting steps are considered, diffusion or solution precipitation (crystallization) of new β silicon nitride phase [4–8].

It has to be noted that the curves corresponding to the time development of the β phase content in the sintered body have an integral character, i.e. in these curves the effects of all possible factors are summarized. The investigator has little or no possibility of measuring and influencing the surface area of β silicon nitride phase, the rate of crystallization, rate of nucleation and of studying their role and contribution to the resulting shape of the α–β silicon nitride phase transformation curve. That is why the interpretation of influences of the above mentioned factors on the α–β silicon nitride kinetics can be ambiguous. The aim of this paper is to study the role of the crystallization rate, nucleation rate and surface area of the β silicon nitride phase in the starting powder by a simple computer simulation. The advantage of such an approach is that the role of particular factors on the phase transformation can be considered individually.

2. Model

The model of the α–β silicon nitride phase transformation used for the present simulation is based on the presumptions as follows.

(i) During the simulation the β silicon nitride phase is the stable one.

(ii) Crystallization (growth) of β silicon nitride phase is the transformation rate controlling step.

(iii) The growth of both α and β phase particles is described by [9]

$$r(t)^2 - r(0)^2 = R_k t \tag{1}$$

where $r(t)$ is the particle radius at time t, $r(0)$ the particle radius at time 0, R_k the crystallization rate defined as $R_c = Kc_0\gamma\Omega^2/RT$, where K is the transfer factor dependent on temperature T, c_0 the concentration of new phase at a planar interface, γ the specific free energy of the particle–matrix interface, Ω the molar volume of particle phase, R the universal gas constant and T the absolute temperature.

(iv) All β silicon nitride particles and the α silicon nitride particles with radii larger than or equal to the critical one ($r^* = (\frac{9}{8})\bar{r}$, [9], $\bar{r}$ is the mean particle size) are growing.

(v) Each β phase silicon nitride particle and α phase silicon nitride particle larger than the critical one are growing only at the expense of the nearest small α silicon nitride particle.

(vi) The diminution of radius of small α silicon nitride particles ("decomposition") is also taken into account, the α phase silicon nitride particles smaller than r^* decompose according to Equation 1 at a rate which is a fraction of the crystallization rate.

(vii) The β silicon nitride phase grows on the β silicon nitride particles present in the "green body" at the beginning of the simulation and on the new β

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* *Present address*: Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium, Heisenbergstraße 5, W-7000 Stuttgart 80, Germany.

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silicon nitride particles, if these are nucleated during the simulation.

(viii) The needle-like β silicon nitride particles grow in the direction of the c axis at a rate R_c and in the perpendicular direction at a rate $R_c/2$.

(ix) The growth of β phase needle-like silicon nitride particles is limited by the dimension of the largest pore, which is supposed to be proportional to the largest α silicon nitride particle.

(x) The rearrangement of particles during the simulation is not taken into account (i.e. the distances between the centres of particles are constant).

2.1. Computer simulation

The computer program can be formally divided into two parts.

(I) "green body" formation,

(II) phase transformation and grain growth.

The first part, "green body" formation, includes the random location and size distribution of α silicon nitride particles (spheres, denoted by circles in the figures) and given starting content of β silicon nitride particles (hexagonal prisms, denoted by oblongs in the figures). The surfaces and volumes of particles are calculated in three-dimensional space. The second part, phase transformation and grain growth, includes the growth of β and large α phase silicon nitride particles, the formation of new β silicon nitride particles ("nucleation") and diminution of small α silicon nitride particles ("solution" and "decomposition"). The block diagram of the simulation is shown in Fig. 1.

The free parameters of the simulation are as follows.

(i) Maximum particle radius ($r_{\max}/m$ determines the maximum value of random size distribution of particles).

(ii) Seeding (ξ wt % determines the weight content of the β phase silicon nitride particles in "green body").

(iii) The aspect ratio (ar determines the shape and thus surface area of β phase silicon nitride particles in "green body").

(iv) The rate of crystallization ($R_c(\mathrm{m^2 h^{-1}})$ determines the surface area of the particle covered by the new phase during the time unit).

(v) The rate of nucleation ($R_n(\mathrm{m^{-3} h^{-1}})$ determines the number of new β phase nuclei created in the space unit during the time unit).

(vi) The duration of spontaneous nucleation, ($\tau_n(\mathrm{h})$ determines the time during which the β silicon nitride nuclei are created at a rate R_n).

The changes in microstructure can be observed in two-dimensional projection on the screen during the period of simulation. This two-dimensional projection figures all particles which are distributed in the working cell defined by the dimensions of the figure. The depth of this cell is not constant but this is changed with respect to the requirement to avoid the overlaps of the spheres and/or hexagonal prisms. The depth of the cell corresponds to the sum of diameters of the overlapped particles. The distribution of particles within this space can be imaged as a distribution of particles located with fixed x and y coordinates while the coordinate z of each particle is conditioned by the requirement of non-overlapping of the particles. This uncertainty in definition of working cell volume is not serious because the space distribution of particles (density) is not taken into account and evaluated during the simulation.

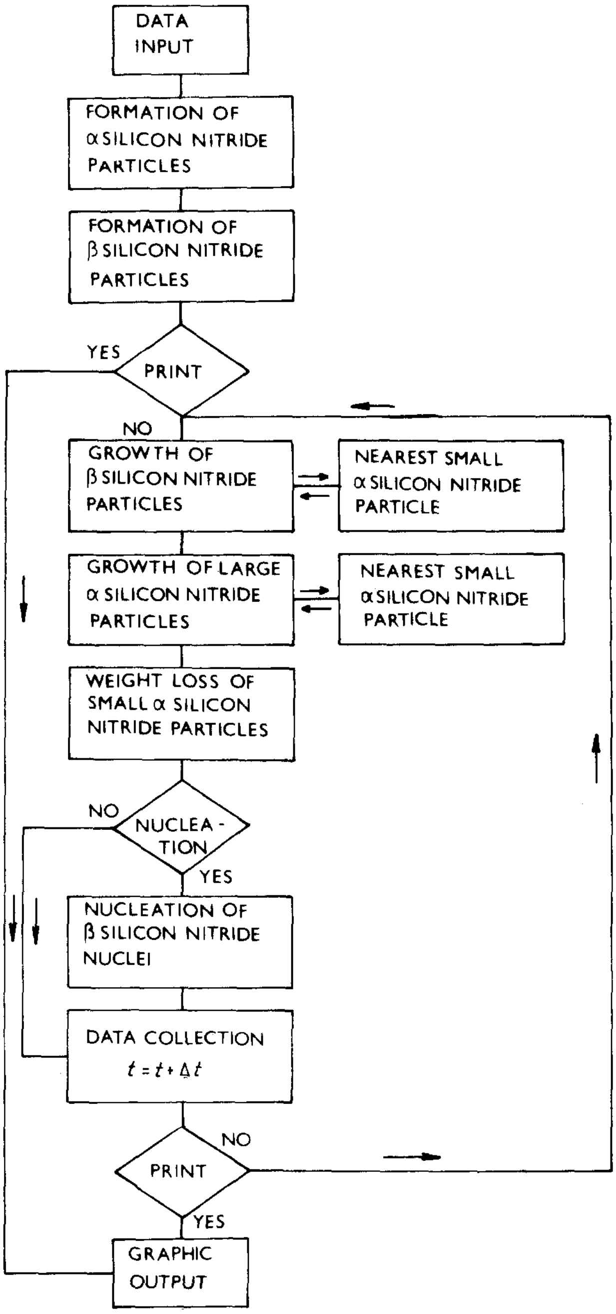

Figure 1 Block diagram of the used computer simulation program.

The simulation also offers a graphic description of the kinetics of α–β phase transformation, weight loss and mean particle radius as a function of time. Other microstructural characteristics are optional. The development of microstructure can be observed during the whole simulation.

3. Results of simulation

The nature of the α–β silicon nitride phase transformation implies that the simulation experiments and their results can be divided into two groups; simulation of the phase transformation (a) without spontaneous nucleation and (b) with spontaneous nucleation.

3.1. Simulation of the α–β silicon nitride phase transformation without spontaneous nucleation

In the present work several simulations were performed, see Table I. The parameters of simulation 1 are listed in Table I. Fig. 2a shows the two-dimensional projection of microstructure of "green body". The total number of particles in the considered space is 93, their mean radius is 0.47 μm. A great decrease in number of small α particles is observable in Fig. 2b which illustrates the status after 1 h of simulation ("firing"). The total number of particles decreases to 51 and mean particle radius increases to 0.64 μm. The small α silicon nitride particles disappeared as a consequence of the decomposition, this is observed as an increase of weight loss at the beginning of the simulation period, Fig. 4b. The status after 10 h of "firing" is illustrated in Fig. 2c, the growth of α and β phase silicon nitride particles is evident and the decrease in number of small α silicon nitride particles in comparison with the status after 1 h (51 as opposed to 35) is not so dramatic as after the first hour of "firing". The size distribution of particles becomes narrower and the microstructure is more uniform. The status after almost 30 h of "firing" is shown in Fig. 2d. The number of particles is practically the same as in Fig. 2c (35 as opposed to 33) and the mean particle radii are also almost the same (0.81 as opposed to 0.83 μm).

TABLE I

Simulation	ξ (wt %)	ar	R_c ($\mu m^2 h^{-1}$)	R_n ($10^{15} m^{-3} h^{-1}$)	τ (h^{-1})
1	20	1	0.1	0	0
2	10	1	0.1	0	0
3	10	1.5	0.1	0	0
4	10	1	0.25	0	0
5	10	1	0.01	0	0
6	10	1	0.1	6	3
7	10	1	0.3	3	3
8	10	1	0.3	1	3
9	10	1	0.1	3	3

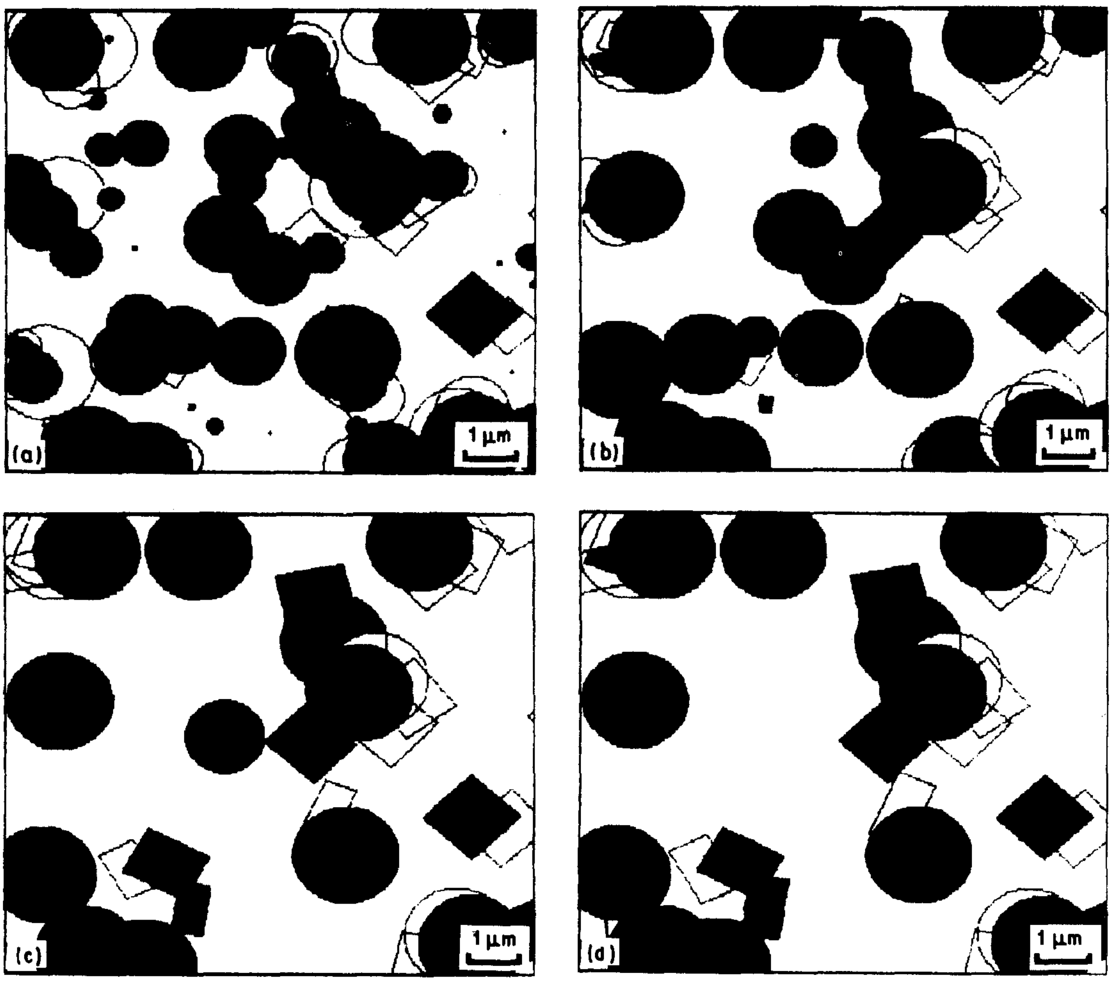

Figure 2 Simulated "microstructure" of the: (a) "green body", (b) after 1 h of "firing", (c) after 10 h of "firing" (d) after 29.9 h of "firing" without spontaneous nucleation.

The higher starting content of β phase silicon nitride particles in "green body", 20 mass %, (simulation 1, Table I) as opposed to 10 mass %, (simulation 2, Table I) results in a higher content of β phase after the "firing" period, Fig. 3a as opposed to Fig. 3b. A higher starting β phase content also results in a higher rate of phase transformation (higher slope of transformation curve), Fig. 3a. Both these findings are considered to be the consequence of a higher free surface area of β silicon nitride phase in the case of higher weight content of β phase. In order to confirm this assumption, Fig. 3c shows the time changes in the β silicon nitride phase content when the starting amount of β phase is 10 mass %, the same as in the case figured in Fig. 3a but the free surface area of particles of this phase is about 30% higher, simulation 3, Table I. The resulting α–β silicon nitride phase transformation curve is similar to those, figured in Fig. 3a. This means that the free surface area of β silicon nitride particles, not the absolute weight content of these particles is dominant for the absolute value of final β phase content and for the rate of phase transformation. Fig. 4a, b and c show the weight loss curves of above discussed simulations, the differences are obvious. These differences are the consequence of different microstructures resulting from the different starting content and shape distribution of β phase silicon nitride particles. The comparison of two weight loss curves (Fig. 4b as opposed to Fig. 4c) implies, that, the finer β phase particles distributed in the "green body" result in lower weight loss.

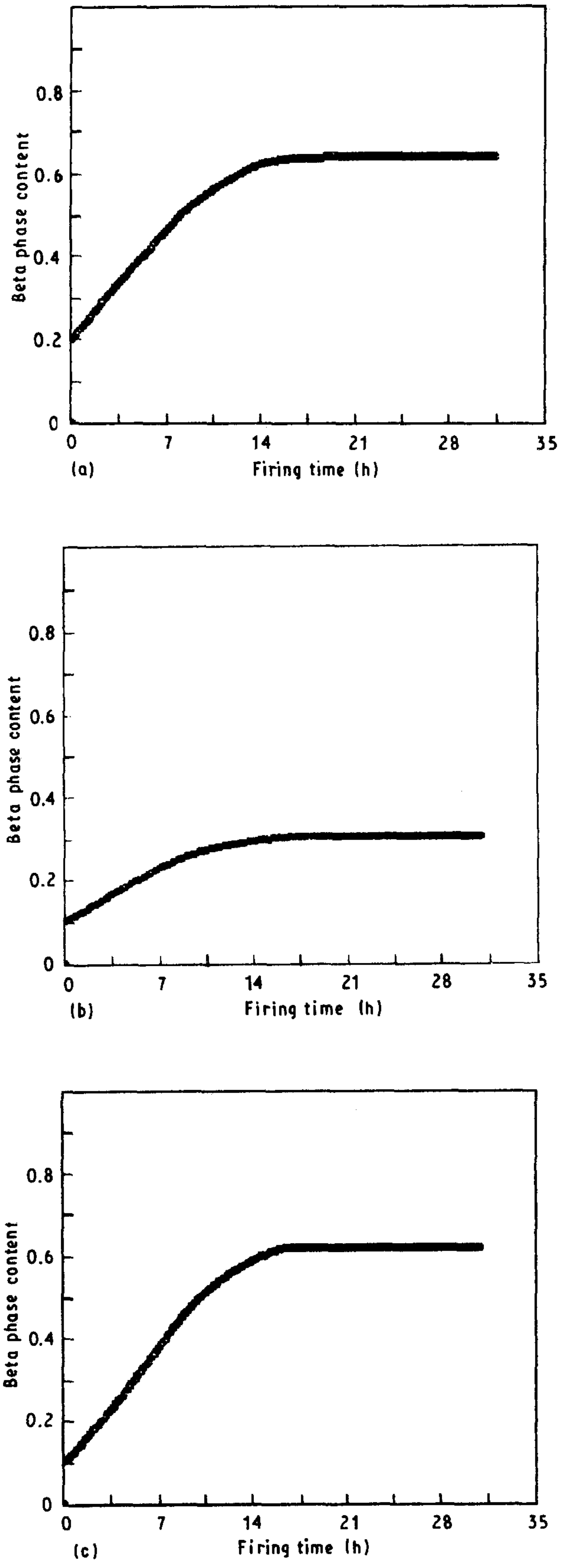

Figure 3 β-silicon nitride phase content transformed during the: (a) simulation 1, (b) simulation 2, (c) simulation 3, Table I.

All the above mentioned simulation experiments were done with the same value of crystallization rate. The value of R_c is a function of material constants and the temperature. Crystallization rate is increasing with increasing temperature because of temperature dependence of transfer factor. According to Equation 1 the effect of temperature on the phase transformation and weight loss is expressed only by the crystallization rate. Fig. 5a corresponds to the case of simulation 4 when the rate of crystallization is $R_c = 0.25\ \mu m^2\ h^{-1}$ while in the case shown in Fig. 5b, the value of R_c is $0.01\ \mu m^2\ h^{-1}$, simulation 5. The difference in the rate of phase transformation is evident. The higher weight loss in the case of higher rate of crystallization, Fig. 6a in comparison with weight loss curve corresponding to the lower R_c, Fig. 6b, is the result of the application of higher "temperature".

Finally, on the basis of the above simulation results, it can be concluded that the behaviour of the suggested model is reasonable. The most important factor determining the α–β silicon nitride phase transformation (in the case without spontaneous nucleation) is the free surface area of the β phase silicon nitride particles present in the "green body".

3.2. Simulation of α–β silicon nitride phase transformation with spontaneous nucleation

As was mentioned above, the rate of nucleation is defined as the number of new stable β silicon nitride nuclei created per unit time in space unit. This rate is generally not a constant function of time. A simple approximation of this function was used in the present simulation. The nucleation rate is constant during the limited period of simulation, after some time period of simulation the rate of nucleation falls to zero.

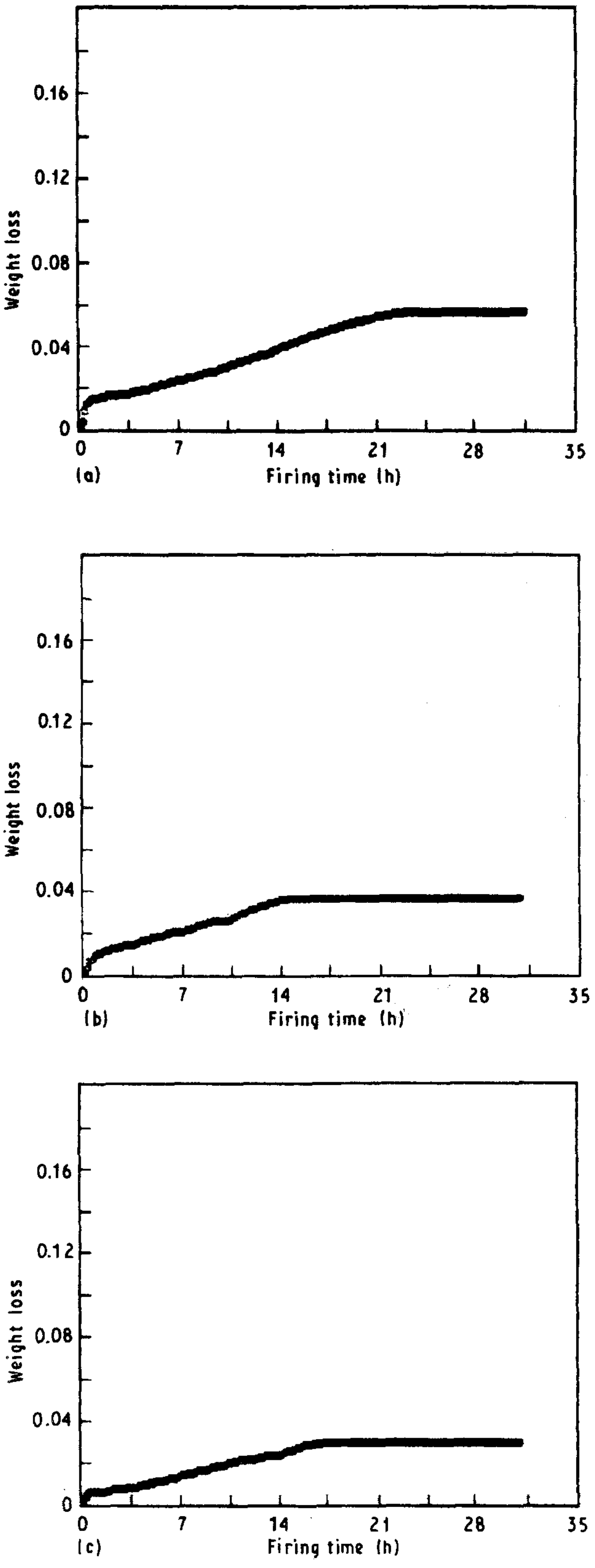

Figure 4 Weight loss of "fired body" corresponding the: (a) simulation 1, (b) simulation 2, (c) simulation 3, Table I.

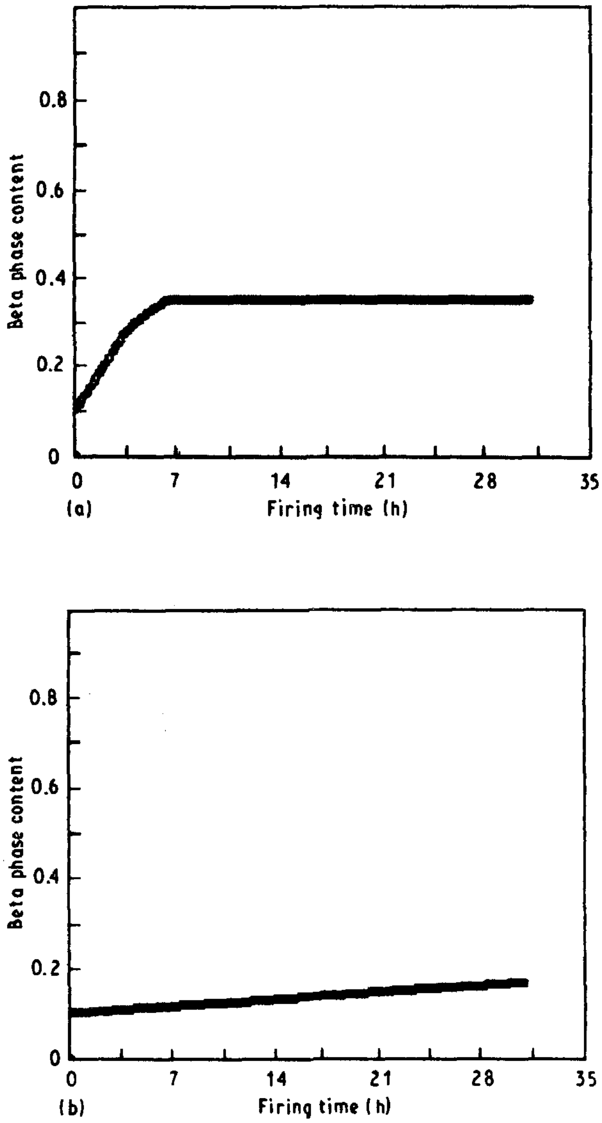

Figure 5 β-silicon nitride phase content transformed during the: (a) simulation 4, (b) simulation 5, Table I.

When spontaneous nucleation occurs, the microstructure is developed in a rather different way. Fig. 7a shows the simulated microstructure of "green body" (simulation 6, Table I) with 103 particles per volume considered. The mean particle radius is 0.45 μm. The status after 1 h of firing is illustrated in Fig. 7b. The microstructure, difference in total number of particles and mean particle radius are similar to the simulations shown in Fig. 2a and b. The growth of β and α silicon nitride particles is observable after 10 h of "firing", Fig. 7c. The creation of β silicon nitride nuclei influences the total number of particles which is higher (75) than the number of particles after 1 h of "firing" (69). The microstructure after 10 h of "firing" is finer (mean particle radius is 0.73 μm) as in the case shown in Fig. 2c where the mean particle radius is 0.81 μm. The final microstructure after almost 30 h of "firing", Fig. 7d, is also slightly finer (mean particle size radius is 0.79 μm) as in the case shown in Fig. 2d where the final mean particle radius is 0.83 μm, but the difference is not as high as that after 10 h. On this basis, it can be concluded that the microstructure development is different to the case when no spontaneous nucleation is present, i.e. the β silicon nitride phase nuclei formed shift the particle size distribution toward the lower values.

The α–β silicon nitride phase transformation in the presence of spontaneous nucleation is more complex, the free surface area of β silicon nitride phase grows up because of spontaneous nucleation, the changes in

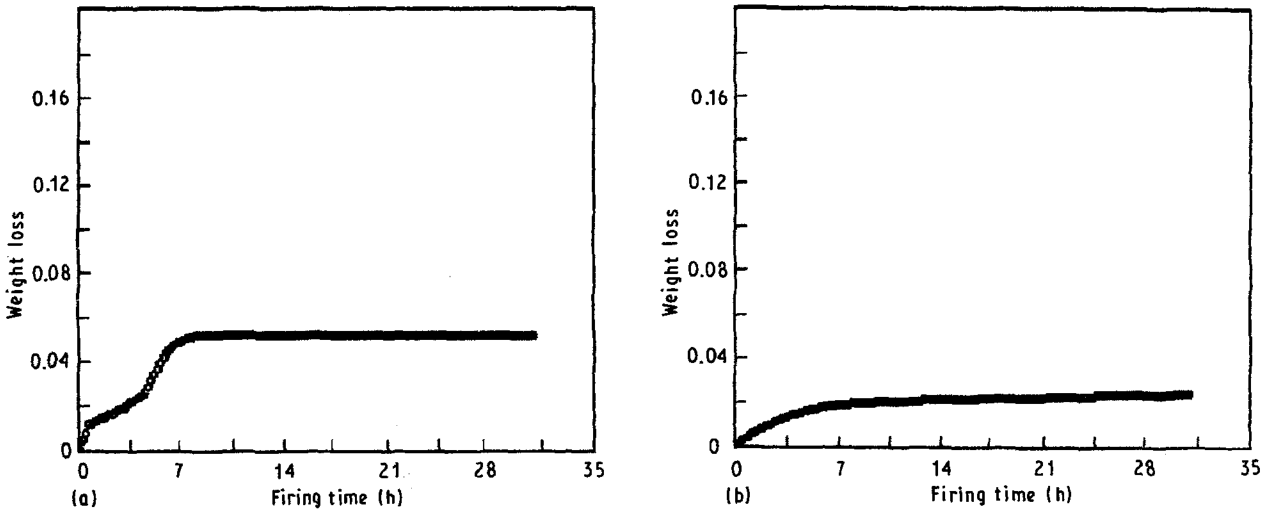

Figure 6 Weight loss of "fired body" corresponding the (a) simulation 4, (b) simulation 5, Table I.

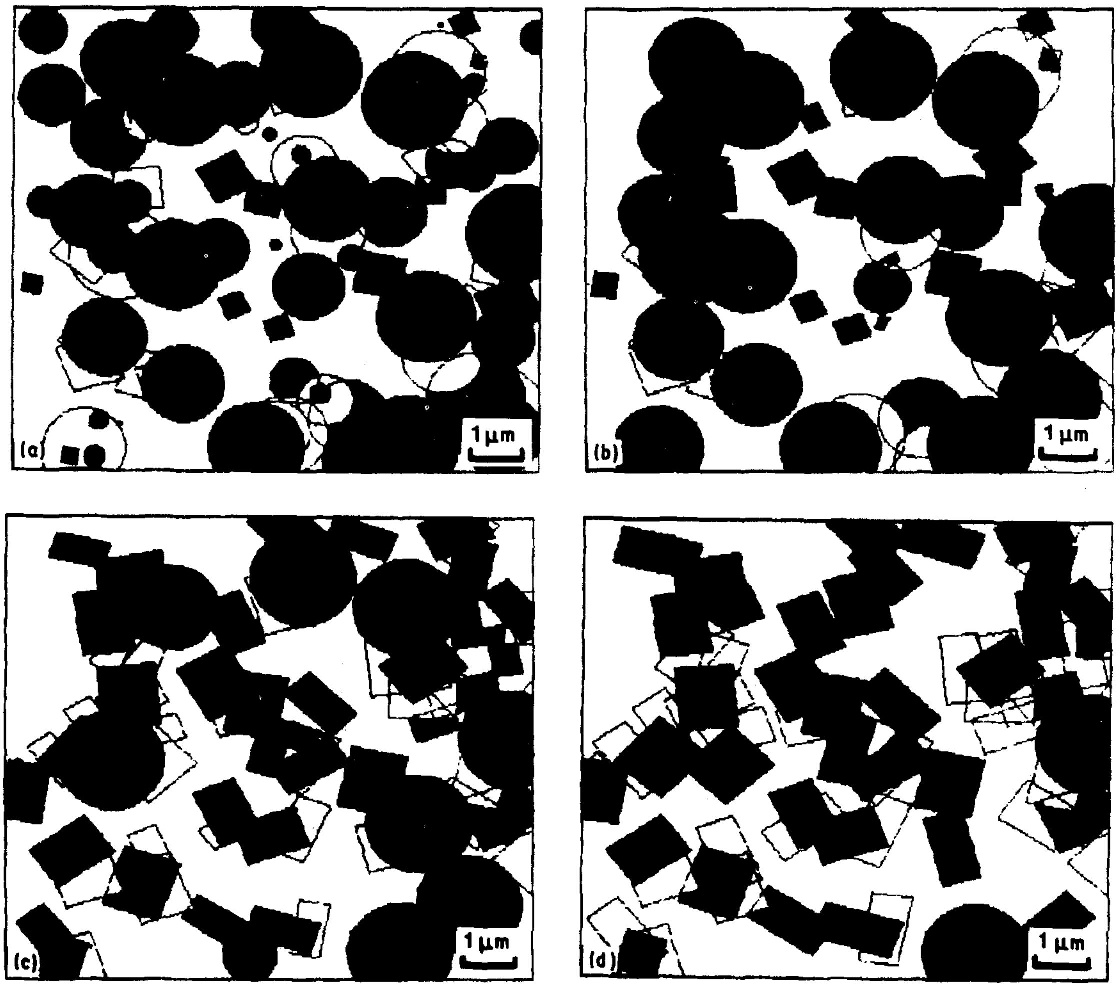

Figure 7 Simulated "microstructure" of the (a) "green body", (b) after 1 h of "firing", (c) after 10 h of "firing", (d) after 29.9 h of "firing" with spontaneous nucleation.

microstructure are strongly influenced by this nucleation. The resulting transformation curve is an integral curve of two processes, crystallization and nucleation. An attempt to consider the role of particular processes is demonstrated in Fig. 8a, b and c. Fig. 8a and b corresponds to the phase transformation kinetics which resulted from simulations 7 and 8, respectively, Table I. The slopes of both curves prior to reaching the maximum value of β silicon nitride phase content are the same. This means that the rate of crystallization is dominant in the beginning of the transformation while the excess of surface area of β silicon nitride phase due to nucleation is not so expressive. The rate of nucleation strongly influences the absolute value of β silicon nitride phase content, the maximum value of β silicon nitride phase content in

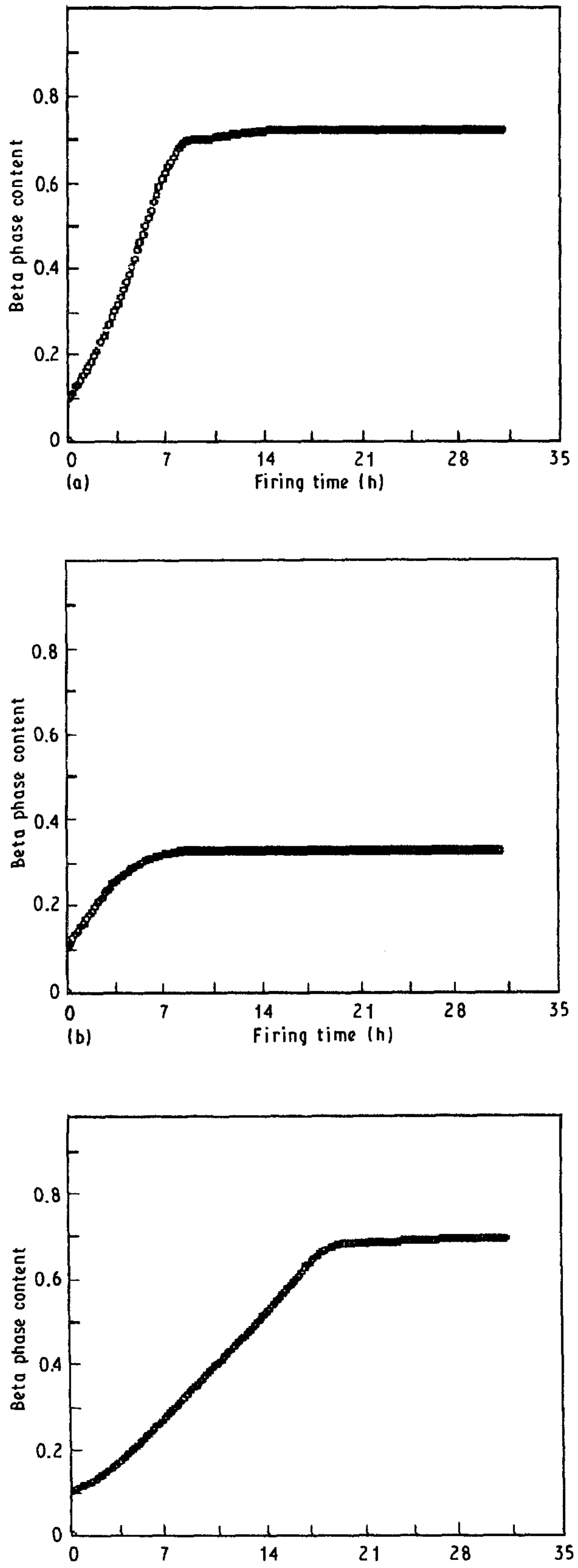

Figure 8 β-silicon nitride phase content transformed during the: (a) simulation 7, (b) simulation 8, (c) simulation 9, Table I.

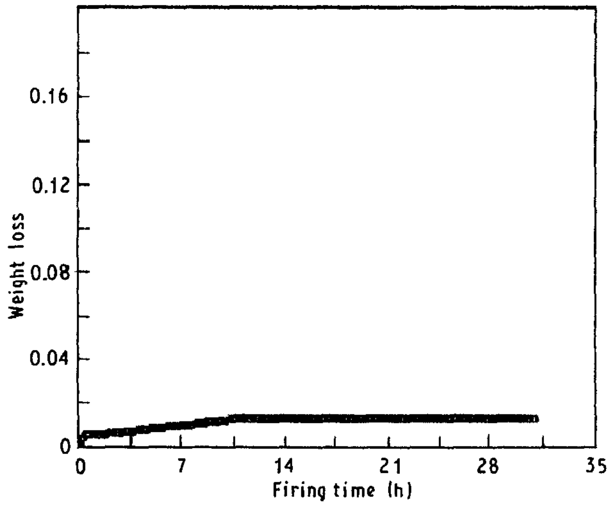

Figure 9 Weight loss of "fired body" corresponding to simulation 9, Table I.

the case of higher rate of nucleation is over 70 mass % but in the case of lower rate of nucleation this value is less than 40 mass %, Fig. 8a and b. The simulation of phase transformation, the result of which is shown in Fig. 8c is characterized by the same parameters as simulation which results in Fig. 8a, the only difference is in the rate of crystallization, this is three times lower, simulation 9, Table I. The maximum value of β silicon nitride phase content is in both cases almost the same, i.e. the free surface area of β silicon nitride phase created within the period of spontaneous nucleation is almost the same. Only the slope of curve in Fig. 8c is smaller, this is directly caused by the lower rate of crystallization.

The difference in microstructure results in a difference of weight loss curves. Fig. 9 shows the weight loss curve corresponding to the simulation 9, Table I. In comparison with Fig. 4b (simulation 2, Table I) the total weight loss is lower in the case with spontaneous nucleation during "firing". This tendency is also observed experimentally, but it must be noted here, that present results cannot be directly compared with experimental measurements because the decomposition rate is also influenced by other parameters such as chemistry of bed composition, liquid phase, starting powder and consolidation technique used.

4. Discussion

As previous simulations showed, the most important factor limiting the phase transformation, final microstructure and weight loss is the free surface area of β silicon nitride phase in silicon nitride "green body". A similar result was observed experimentally when the synthesis of α silicon nitride powder by carbothermal reduction of silica was investigated [10]. This study confirmed that the refinement of α silicon nitride seeds (enlargement of this free surface) in the starting mixture causes an increase in the conversion rate during the synthesis of these powders. The synthesis of α silicon nitride powder is, nevertheless not the phase transformation; the role of seeds in both cases is rather similar. This result supports the declared presumption of present simulation that the crystallization, not the diffusion, is the phase transformation controlling mechanism. In principle, the free surface area of the β silicon nitride phase can be varied by the starting content of β phase seeds with defined morphology and by the rate of nucleation, i.e. in reality by the morphology of β silicon nitride particles present in the silicon nitride powder prior to firing and by the firing temperature and chemistry of the sintering additives. The important result of the present simulation is that development of the microstructure (particle size distribution) with and without the presence of spontaneous nucleation is rather different. This phenomenon is obvious from experimental observations and justifies the applicability of the present model. The role of the important factor, the particle size distribution of silicon nitride powder used is not taken into consideration. This is an individual characteristic and changes according to the production method of the silicon nitride powder used. The present simulation experiments used the random size distribution of particles with maximum particle size of 2 μm. The present approach, without particle rearrangement, is acceptable when the positions of the particles in the powder body are rigid during the period of simulation. In reality, this can correspond to the firing of silicon nitride powder body without sintering additives and also in the case when these additives are used but the diffusion is fast enough and the crystallization is the rate controlling step. During the simulation the spontaneous nucleation was and was not considered, in order to approach the reality. It is supposed that the spontaneous nucleation is negligible in the case when during the firing of silicon nitride green body no sintering additives are applied. On the other hand, it is supposed that the presence of a liquid phase at the sintering conditions favours the spontaneous nucleation.

Finally, it must be admitted that the present model is based on one controversy. The α silicon nitride phase is defined as unstable. On the other hand the large α silicon nitride particles are growing, not decomposing. The stability status of the α silicon nitride particle is defined only by the dimension of the α particle. This could lead to the feeling that it is impossible to reach complete α to β silicon nitride transformation. In the case when the spontaneous nucleation is large enough all α silicon nitride particles are, however, converted to the β phase modification because the large β silicon nitride particles take on the role of critical radius determining particles.

Generally, the present simulation model after some minor corrections is applicable in the study of the various systems undergoing phase transformation and/or in the investigation of kinetics of the synthesis of powders.

The perspective of the present model is its development with respect to the particle rearrangement during the simulation. In this case it will be possible to consider also diffusion as the phase transformation controlling step.

5. Conclusions

Computer simulations based on the present model implies the conclusions are as follows.

The rate of α–β silicon nitride transformation grows with crystallization rate ("temperature") and with enlargement of free surface area of β silicon nitride phase present in "green body" prior to "firing" and with rising of the rate of nucleation.

The limiting value of β silicon nitride phase content at the end of the simulation is influenced only by the total free surface area of β phase silicon nitride particles in "firing body". Size of this area depends on the shape, content of β silicon nitride particles in "green body", and by the duration and rate of spontaneous nucleation.

The presence of spontaneous nucleation during silicon nitride phase transformation results in rather different development of microstructure.

The weight loss is the result of microstructure (i.e. particle size distribution within the "fired body") and crystallization rate ("temperature"). A larger number of small α silicon nitride particles with dimensions under the critical radius r^* results in the higher weight loss under the same "temperature". Higher "temperature" produces the higher weight loss.

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