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Advanced HT Ceramic Materials via Solid Combustion

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Abstract

Factors which control the run of solid combustion in the carbide- and nitride-yielding systems and the properties of the products are reviewed. Emphasised is the role of reactant particle size, of thermal conductivity of particulate reactants bed and of the appearance of a transient liquid. Several examples are given of a production by solid combustion (SHS) and successful use of single phase and composite powders of refractory carbides and nitrides to obtain a wide range of advanced HT ceramic materials such as nanolaminates, nano/micro composites and materials having an interpenetrating (duplex) microstructure. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: SHS, solid combustion, composites, carbides, nitrides.

1 Introduction

Materials technologies should aim at production of materials which have optimum properties for performing specified functions. In ceramic technology (powders⇒shaping⇒sintering/hot-pressing⇒component) this goal can be attained by appropriate phase composition and microstructural design provided high quality powders are used. A large number of methods for producing such powders has been developed but they are mostly sophisticated and often not cost-, energy-, and time-efficient (Table 1). Therefore, many of the methods have a lower potential in terms of sustainable development[1–3] than versatile methods which show these features. Combustion synthesis or self-propagating high-temperature synthesis (SHS) originated by Merzhanov and Borovinskaya[4] belongs to the latter category.

The advantages of solid combustion are particularly evident in synthesis of refractory carbides and nitrides by reactions of metallic with non-metallic elements.[6–9] The reactions in such heterogeneous systems are usually accompanied by formation of a nitride or carbide reaction layer between the reactants. Because the diffusivity in carbides and nitrides is generally low the growth in thickness of the layer with time constitutes a diffusion barrier slowing down the conversion rate. Therefore, high temperatures and long times of heating are usually necessary for carbide and nitride synthesis under conventional conditions. Because the thickness of the reaction layer at late stages of the reaction is proportional to the initial reactant particle size their fine size is also usually required.

The specific mechanism of reactions and transformations on solid combustion in carbide and nitride systems permits to by-pass this obstacle and produce in a rapid and rather simple way single and composite carbide and nitride-based powders which can be used to produce advanced HT ceramic materials. However, to realise the method in a controlled manner notice is to be taken of some factors specific to solid combustion synthesis of carbides and nitrides. These are not a matter of common knowledge and their discussion shall precede a description of the particular solid combustion-derived powders and materials produced from them.

2 Some Factors Controlling the Run of Solid Combustion in Carbide- and Nitride-Yielding Systems

2.1 Particle size of the reactants and thermal conductivity of their particulate bed

In solid combustion synthesis the main source of heat required to carry it out are exothermic reactions between the reactants. The heat produced by the reactions, once initiated by external heat sources, can bring about a flash-like temperature increase in the system, i.e. its ignition, provided that the heat production rate exceeds heat loss rate to the environment and colder parts of the system. A high reaction enthalpy is, therefore, required and it has been found that solid combustion can be

Table 1. Features of some methods for producing high quality powders and the characteristics of the powders (after Ref. 5)

Method	*Furnace synthesis*	*Co-precipitation from solutions*	*Hydrothermal synthesis*	*Synthesis in the gas phase*	*Carbothermal reduction*	*Combustion methods*
Characteristics of the powder:						
Purity	Low	High	High	Medium to low	Medium to low	Medium to high
Small particle size	Not	Yes	Yes	Yes	Yes–not	Yes
Compositional control	No	Good	Good	Medium	Medium	Medium
Features of the method:						
Low cost of installations	Yes	Not	Not	Not	Not	Yes
Low cost of reactants	Yes	Not	Not	Not	Yes	Not–yes
Consumption of external energy sources	High	High	High	Medium	Medium	Low
Short time of synthesis	Not	Not	Not	Yes	Not	Yes
Simplicity and low number of main processing steps	Yes	Not	Not	Not	Not	Yes
Main applications:	Powders of low quality	Powders of simple and complex oxides	Powders of simple and complex oxides	Powders of simple covalent compounds	Powders of simple covalent compounds	Powders of covalent and intermetallic compounds

realised in systems where the enthalpy is of the order of 100 kJ mol^{-1} or higher.[6] Very many reactions giving rise to crystalline carbides and nitrides fall into this category. Another feature of solid combustion is a self-sustaining propagation of the hot zone originated by ignition. Besides the reaction enthalpy this is controlled mainly by the reactants' particle size and thermal conductivity of their particulate bed.

By way of example let us consider the role of these factors in silicon containing systems in which silicon carbide and silicon nitride are produced. Let us start with the role of the particle size of the non-metallic reactant, carbon, in the Si + C system in which the reaction: Si (s,l) + C(s) = SiC(s) takes place. Figure 1 illustrates for a typical porous bed of particulate Si + C reactants the temperature versus distance from the ignition site after different times as it occurs at various carbon particle sizes. It indicates that in contrast to synthesis by conventional heterogeneous solid-state reactions a very fine size of the carbon reactant is not required and

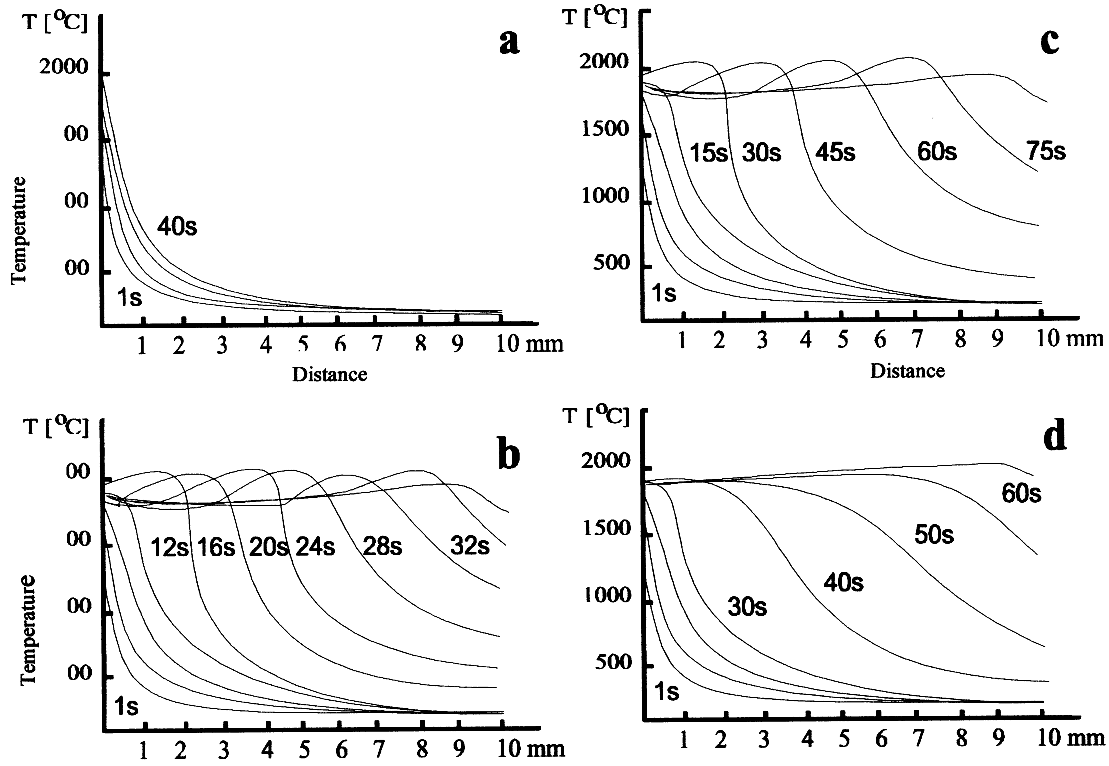

Fig. 1. Temperature versus distance from the ignition site after different times (in s) calculated for porous beds of particulate Si + C reactants at various carbon particle size, r, and thermal conductivity of the bed, λ (after Ref. 10 Remarks: (a) $r = 1\,\mu$m, $\lambda = 0{\cdot}48$ W mK^{-1}; (b) $r = 1\,\mu$m, $\lambda = 0{\cdot}96$ W mK^{-1}; (c) $r = 5\,\mu$m, $\lambda = 0{\cdot}48$ W mK^{-1}; (d) $r = 5\,\mu$m, $\lambda = 0{\cdot}96$ W mK^{-1}.

not advantageous. Namely, fine particles lose heat to the environment more readily than larger ones and this is equivalent to a decrease of the thermal conductivity of the porous particulate bed and inhibition of a self-sustaining propagation of the hot (combustion) zone. The effect of a too small particle size can be offset by an increase of the thermal conductivity of the bed. For a given system this is equivalent to an increased packing density of the particles. The effect of thermal conductivity is also illustrated in Fig. 1 and additionally in Fig. 2 for another system of reactants.

For the metallic reactant, silicon, a small size of particle is required. In the overwhelming majority of carbide-yielding systems the ignition temperature coincides with the melting point of the metallic reactant.[11,12] This is believed to be due to a substantial increase of the intensity of the reaction when the contact area becomes suddenly increased by spreading of the molten metal or its alloy over the surface of the non metallic reactant particles. For reasons which are not entirely clear yet the coincidence of the melting point and ignition is observed if the particle size of the metallic reactant is not too small. To cite an example, ignition in the Si–C system occurs at the melting point of silicon only if the equivalent diameter of its particles is larger than 0·64 μm.[8]

The role of the particle size of the metallic reactant melting during solid combustion has been investigated also in case of filtration combustion in the Si(s,l)–N_2(g) system which yields silicon nitride by the reaction $3Si + 2N_2 = Si_3N_4$. In order to sustain the reaction and to obtain a stable propagation of the hot (combustion) zone the Si (s,l)-N_2 (g) interface area has to remain extended, viz. a coagulation of molten silicon particles has to be prevented. This is feasible if the Si particles melt only superficially and a thin discontinuous crust of Si_3N_4 is formed on the surface of the Si particles. constituting a solid skeleton which hampers the coagulation. Calculations backed by experiments have shown that under typical conditions of solid combustion in the filtration regime in the Si(s,l)–N_2(g) system (velocity of propagation of the hot combustion zone equal to 0·2–0·8 cm min^{-1}, rate of temperature increase equal to 150°C/s^{-1}, nitrogen pressure of 3 MPa) this occurs at a size of the starting Si particles between 60 and 100 μm.[13]

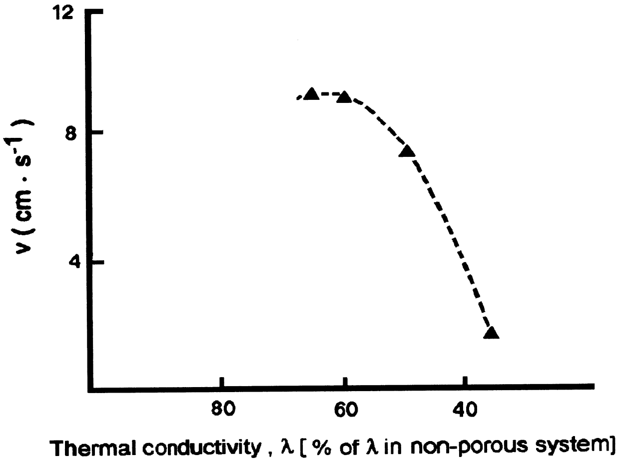

Fig 2. Velocity of self-propagation of the hot (combustion) zone versus the thermal conductivity of the particulate bed of Ni–Al reactants (after data quoted in Ref. 11).

2.2 The 'migrating thin reaction layer' mechanism

Formation of a liquid phase by melting of the metallic reactant or low-melting eutectics permits reaction mechanisms to occur which explain the very rapid reaction and conversion rates observed on solid combustion in carbide- and nitride-yielding systems. Some clues as to these mechanisms have furnished studies into solid combustion in the Si–C system. Under conditions of solid combustion the single Si (s,l,g) + + C(s) = SiC (s) exothermic reaction which takes place here is able to raise the temperature to 1950–2150°C and the resulting silicon carbide forms metamorphoses of the original carbon particles, irrespective of whether they are fibres, carbon black or charcoal.[14,15] This indicates that on solid combustion takes place an inward diffusion of silicon through the reaction product layer (SiC) to the C/SiC interface. Similar observations have been made also in investigations using single-crystal silicon.[16,17]

At the temperature of solid combustion between 2000 and 2200°C can take place a dissolution of the solid product, SiC (or of carbon) in liquid silicon or its alloys formed about 1410°C. Experimental diffusion and dissolution data used in an appropriate kinetic model have permitted to conclude that at these temperatures a dynamic equilibrium is established in which the reaction layer (primary SiC) is growing at the C/SiC interface and simultaneously dissolving at the SiC/Si(l) interface at the same rate.[18] Due to this the thickness of the initially thin reaction layer does not grow with time and the thin reaction layer is migrating into carbon particles pulling in its wake a solution of carbon in liquid silicon. The liquid solution becomes eventually supersaturated and the final product, secondary silicon carbide, is precipitated from the solution (Fig. 3). A mechanism akin to this 'migrating thin reaction layer' has been observed in the electron microscope during initial stages of rapid heating, simulating solid combustion, in other metal–carbon systems such as Ti-C, Nb-C, Ta-C.[19]

Such a mechanism seems to be more widespread. Namely, a persistence of a thin reaction layer and

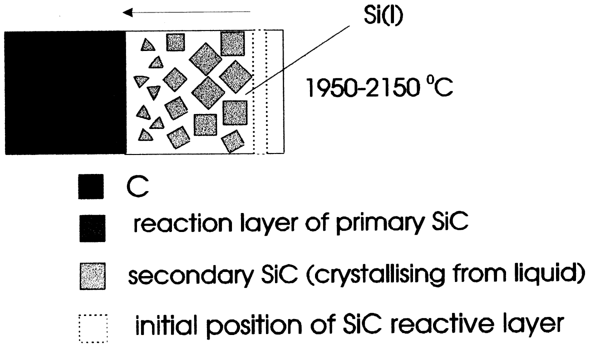

Fig. 3. Mechanism of reactions and transformations on solid combustion in the reactive Si–C system. At the peak temperature of solid combustion (1950–2150°C) a 'migrating thin reaction layer' mechanism occurs: a thin SiC reaction layer is migrating into carbon particles pulling in its wake a solution of carbon in liquid silicon; when the liquid solution becomes supersaturated with respect to SiC, secondary silicon carbide is precipitated (after Ref. 18).

formation of the final products via solution–precipitation is also very probable on solid combustion in systems yielding intermetallic compounds. This is due to the fact that the rate of dissolution of metals in liquid alloys is equal to or higher than the rate of growth of the reaction layer.[20] The mechanism of reactions and transformations which is believed to occur on solid combustion synthesis of TiNi and TiCo in the Ti–Ni and Ti–Co systems is shown in Fig. 4.

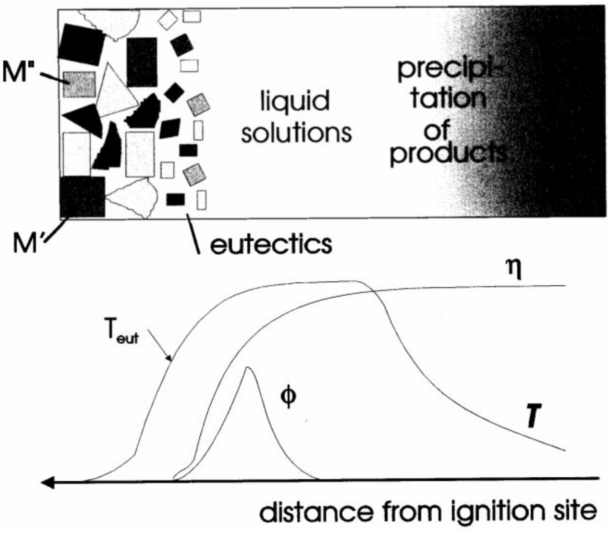

Fig. 4. Schema of reactants interactions on solid combustion in particulate beds of Ti and Ni. Ti and Ni do not melt at the temperatures of solid combustion but low melting eutectics are formed (β-Ti s.s + Ti_2Ni) at T_{eut} which form layers dividing the refractory Ti and Ni particles which eventually disintegrate into smaller ones. The disintegration facilities solution of the reactants in the liquid eutectics while a reaction layer (Ti_3Ni_3, Ti_2Ni_3) remains thin or is absent. The final product is formed by precipitation from the super saturated liquid solution; T, temperature; T_{eut}, eutectic temperature; η, the degree of advancement of the reaction(s); ϕ, function of the heat release rate; M, one metal (e.g. Ti); M,′, another metal (e.g. Ni) (after Ref. 21).

All these observations underline the important role of a transient liquid phase in realisation of the very rapid synthesis of carbides and nitrides by solid combustion. This shall also be demonstrated by the particular examples in the following text.

3 Monophase Carbide and Nitride Powders and Components Produced via Solid Combustion

As previously indicated monophase carbides like silicon carbide and nitrides like silicon nitride are usually combustion synthesised by reactions of, respectively, carbon or nitrogen with silicon and the mechanism involving liquid formation and precipitation of final solid products from the liquid phase should be important here. Transport over the gaseous phase also may take place in the Si–N_2 system. Owing to the high temperature of combustion enthalpy-rich metastable β-SiC and the high-temperature modification β-Si_3N_4 are the products of solid combustion in the Si–C and Si–N_2 system, respectively. The short duration of combustion brings about that the products do not have the final equilibrium composition. This is particularly pronounced with silicon nitride from solid combustion which is nitrogen-deficient.[22] The non-equilibrium composition can be purposefully increased through doping *in situ* by the usual sintering aids such as B and C in case of SiC and Y_2O_3 and Al_2O_3 in case of Si_3N_4 synthesis, respectively. All this gives rise to a different behaviour on sintering of the solid combustion-derived powders as compared with more conventional powders and to a development of a different microstructure in the sintered components.

Compared to conventional powders the solid combustion-derived silicon nitride and carbide start to densify after a longer time of sintering or at a higher temperature, respectively, but their use permits to attain higher ultimate densities of components (Figs. 5 and 6). It should be noted that opinions are still heard about a poor sinterability of solid combustion-derived powders. The possibility to modify the microstructure will be illustrated by the example of sialons. By incorporating e.g. Al_2O_3, Y_2O_3 *in situ* β-sialons can be produced in solid combustion.[9] These powders can attain high densities on sintering already at a temperature of 1650°C which is lower than the one at which exaggerated growth of elongated grains is usually observed in the Si_3N_4-Al_2O_3-Y_2O_3 system (about 1700°C). Due to this the sintered components have a microstructure which consists of small, nearly equiaxial grains[9,25] (see also Table 2). For sialons conventionally produced by sintering of mixtures of a Si_3N_4 and sintering aids such as Al_2O_3, Y_2O_3

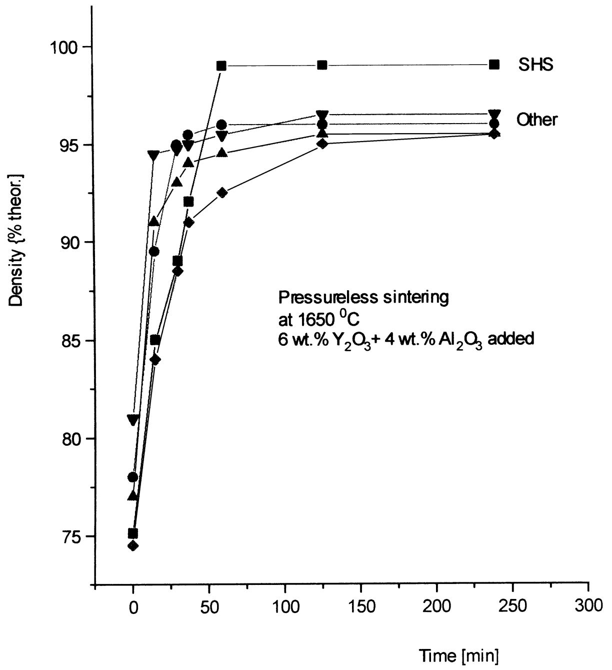

Fig. 5. Density versus time of pressureless sintering at 1630°C of silicon nitride powders containing 6 wt% of Y_2O_3 and 4 wt% of Al_2O_3. The density obtained in case of solid combustion-derived β-silicon nitride-based powder is compared with the one observed with α-silicon nitride-based powders of other origin (after Ref. 23).

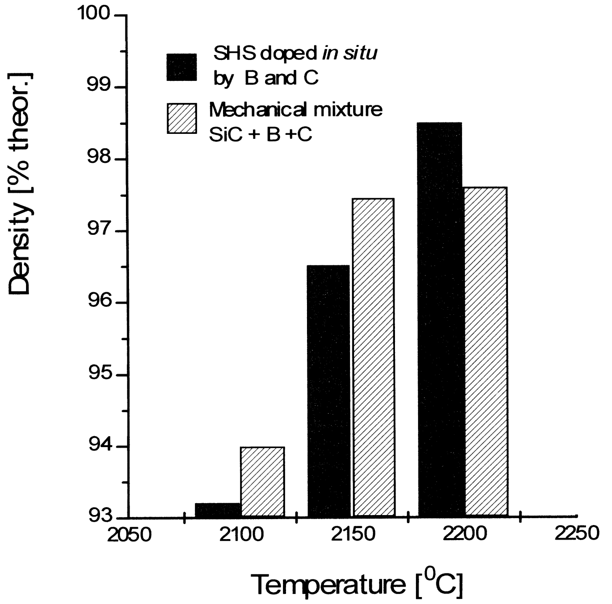

Fig. 6. Density versus temperature of pressureless sintering for 1 h of silicon carbide powders containing sintering aids (0·5 wt% of B and 1 wt% of C) in case of solid combustion (SHS)-derived βSiC powders and mechanical mixtures of αSiC mixed with sintering aids of the same composition and content (after Ref. 24)

and other oxides, a glassy phase at grain boundaries is typical. This phase either does not occur with the combustion-derived material or cannot be detected owing to its small thickness. Instead, a phase having a structure akin to the sialons is observed here.

A plausible explanation of these observations is the following. The nitrogen-deficient structure of the solid combustion products promotes an *in situ* incorporation of Al and O into the silicon nitride lattice on solid combustion. Substantial amounts of Si_2N_2O have been found, indeed, in the solid combustion-derived nitride powder.[26] Si_2N_2O disappears after some time of sintering but according to the phase equilibrium diagram[27] in its presence a liquid phase is formed at a lower temperature than in its absence. Due to this the liquid-assisted sintering which is necessary in the Si_3N_4-based systems can take place at a lower temperature than is the case with mechanical mixtures of Si_3N_4 and $Al_2O_3 + Y_2O_3$.

4 Composite Powders and Components Produced via Solid Combustion

Notwithstanding the encouraging results with the principally one-component powders it seems that solid combustion has even a greater potential for producing composite powders. The advantages of this method are as follows:

1. a less heterogeneous distribution of the components can usually be attained in the powders and this in a more simple way than with other methods;
2. the composition ratio between phases in the powders can be adjusted in a relatively wide range enabling production of a broad range of composite materials by sintering and hot pressing.

4.1 SiC-B_4C composite powders

The particles of powders obtained by solid combustion in the Si–B–C system have been found to consist of alternating SiC and $B_{13}C_2$ nanolayers.[25,28] This brings about a rather homogeneous distribution of silicon, boron and carbon in the powder. The formation of such particles is believed to be due to a run of reactions similar to that previously described for the Si–C system. Namely, the reactions in the Si–C–B system which yield B_4C and solid solutions of boron carbide have a low enthalpy and it can be assumed that the leading, temperature creating reaction is the $Si + C = SiC$ one where the 'migrating thin-reaction-layer mechanism' followed by precipitation from a liquid phase occurs. Boron present in the mixture of reactants can dissolve in the liquid and precipitate in form of nanolayers of $B_{13}C_2$ alternating with the SiC ones.

Owing to the more homogeneous distribution of the constituent elements in the solid combustion-derived powder the composite powders can be

Table 2. Basic parameters of sialon microstructure as produced from solid combustion-derived powders (after Ref. 13)[a]

Sialon type	*Number of grains analyzed*	*Equivalent grain diameter (μ m)*	*Mean β-parameter (measure of grain elongation)*	*Mean α-parameter (measure of development of grain boundaries surface)*
$z - 0{\cdot}5$	660	0·69 ± 0·3	1·34 ± 0·2	1·13 ± 0·12
$z = 1$	580	0·71 ± 0·39	1·32 ± 0·19	1·1 ± 0·19
$z = 3$	540	0·99 ± 0·22	1·35 ± 0·21	1·2 ± 0·09

[a] Remarks: $\beta = d_{\max}/\bar{d}$; $\alpha = P/\bar{d}\pi$ where: $d_{\max}$ is the maximum diameter measured in a direction of the grain; $\bar{d}$ is the mean grain diameter; P is the grain perimeter. The grains are usually considered as elongated if $\beta > 1{\cdot}6$.

produced by using a much simple processing than with other methods (Fig. 7). Moreover, $B_{13}C_2$, is metastable with regard to B_4C and B below about 2000°C and sintering of these powders is accompanied by reactions and transformations such as the spinodal decomposition of $B_{13}C_2$ and reaction of the secondary B with carbon. Therefore, the solid combustion-derived powders have a high chemical activity during sintering that is probably responsible for the high ultimate density of 97 and 99·5 % of the theoretical, respectively, which can be attained by pressureless sintering at 2050°C for 30 min and hot-pressing at 1950°C under 25 MPa for 30 min, respectively. Another advantage of producing the composite powders in the Si–C–B system by solid combustion is the possibility to stretch the composition ratio between phases of the sintered materials in a relatively wide range from 0 to 45 wt % of B_4C without much altering the processing. The microstructures of components obtained by sintering and hot-pressing at different B_4C contents are shown in Fig. 8. It can be seen from the figure that a microstructure of this composite with elongated SiC grains and B_4C inclusions changes at B_4C contents higher than 16–19 vol % to one in which the two phases form

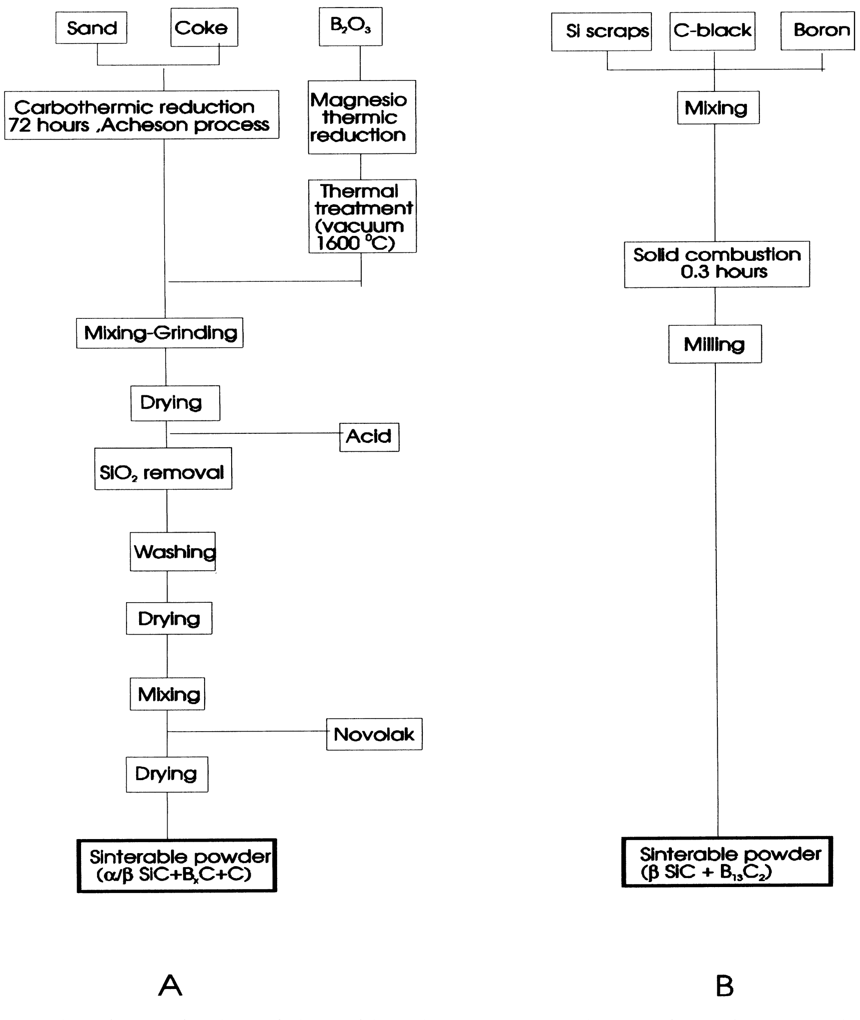

Fig. 7. Flow charts representing the production of sinterable βSiC–B_4C composite powders: (A) conventional preparational route (after Ref. 29); (B) route via solid combustion (after Ref. 6).

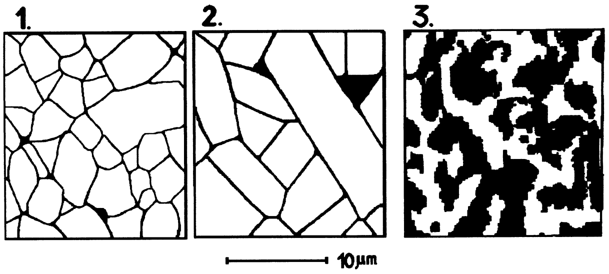

Fig. 8. Binary (computer transformed) microstructure image of βSiC–B_4C composites produced by pressureless sintering at 2050°C for 30 m of solid combustion-derived powders at different B_4C contents: (a) 0·5 vol% B_4C; (b) 7·5 vol% B_4C; (c) 45 vol% B_4C (after Ref. 26) White fields, βSiC; black fields, B_4C.

an interpenetrating (duplex) microstructure. The turning point corresponds to the theoretical percolation threshold which should be reached at 16–19 vol % of the minor constituent.[30]

4.2 Si_3N_4-SiC micro/nano composite powders

To the most widely investigated composite materials belong zero-dimensional or micro/nano-composites recently pioneered by Niihara.[31] One important group form Si_3N_4 (or sialon)/nSiC composites in which SiC nanoparticles, (n)SiC, are dispersed in the polycrystalline Si_3N_4 (or sialon) matrix characterised by grains of the micrometer size. Some of the nanoparticles are dispersed within the grains and some at the grain boundaries. Specially prepared powders had been necessary for producing the Si_3N_4/(n) SiC micro/nano-composites with an adequate microstructure and properties by hot pressing or pressureless sintering. The obvious goal was to get very fine silicon carbide particles and their homogeneous distribution in the silicon nitride (sialon) matrix. According to Ref. 32 this goal has been attained by various sophisticated methods. The methods included consolidation (by pressureless sintering and/or hot pressing) of:

1. amorphous Si–C–N powders;
2. elaborate silicon nitride powders in which the surface oxygen of Si_3N_4 grains was first adjusted by oxidation in air and, next, carbon was coated onto the Si_3N_4 grains by thermal decomposition of CH_4 gas;
3. powders produced by gas phase pyrolysis in mixtures of gaseous $[Si(CH_3)_3]_2NH$ or $[Si(CH_3)_2NH]_3$ and ammonia;
4. powders produced by pyrolysis of Si–C–N polymer precursors;
5. powders prepared from primary Si_3N_4 particles coated by layers obtained by pyrolysis of Si–C polymer precursors. The flow chart of the latter processing is shown in the left-hand part of Fig. 9.

Solid combustion in nitrogen of mixtures of silicon and carbon particles yields composite powders which also can be consolidated by sintering and/or hot pressing to materials having a similar microstructure to the above mentioned. However, simpler starting materials and processing can be used. This is due to the fact that most of the SiC particles formed on solid combustion in these systems already have the desired nanometric dimensions. Again, the versatility of solid combustion

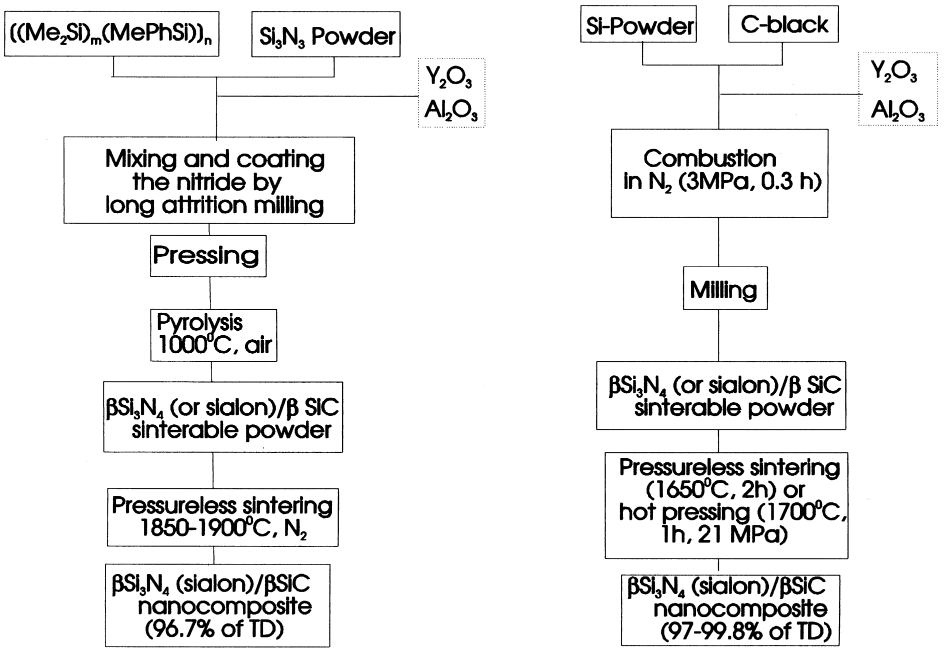

Fig. 9. Flow charts representing the production of Si_3N_4/(n)SiC micro/nano composites from powders; left-hand flow chart for powders derived from the organoelement precursors after Ref. 32; right-hand flow chart for solid combustion-derived powders.

has permitted to vary the composition of the solid combustion-derived powders in wide limits without changing the relatively simple processing, the flow chart of which is shown in the right-hand part of. [9] Namely, from powders produced by solid combustion in reactant mixtures containing low amounts of carbon and yielding up to 15 vol% of SiC, microstructures have been obtained which are typical of Niihara's Si_3N_4/(n)SiC composites. After raising the content of (n)SiC particles above the theoretical percolation threshold (16–19 vol%) by increasing the carbon content in the reactant mixtures, the solid combustion-derived powders have yielded Si_3N_4–SiC powders which permit to obtain composite materials having a duplex (interpenetrating) microstructure. A further increase of carbon content in the reactant mixture to 40 and more vol% has permitted to produce by solid combustion under 3 MPa of nitrogen pressure a single-phase, fine silicon carbide powder only. Namely, at these carbon contents and nitrogen pressure the temperature of solid combustion exceeds 1800°C at which the reaction $Si_3N_4(s) + 3C(s) \Longleftrightarrow 3SiC(s) + 2N_2(g)$ shifts to the right (Fig. 10).

4.3 Complex carbides

Combustion synthesis may be successfully used for fabrication of powders of complex carbides among which deserves special attention Ti_3SiC_2. Its structure confers a set of unusual properties which are not typical of any metallic, ceramic or polymeric material. For instance, Ti_3SiC_2 being highly oxidation-resistant, shows also a reasonably good electric conductivity, plasticity and is as readily machinable as graphite and wood, the other mechanical properties being intermediate between advanced structural ceramics and metallic alloys.[34–39]

In much the same manner as the carbides described earlier Ti_3SiC_2 is believed to form on solid combustion in mixtures of Si, C and Ti via a liquid phase.[37,40] The original constituents can dissolve in low melting titanium and silicon-rich eutectics and precipitate from this liquid. However, due to the short dwelling time at high temperature the stoichiometric 3Ti:Si:2C mixtures yield on solid combustion a product which besides Ti_3SiC_2 contains non-negligible amounts of TiC_{1-x} and $TiSi_2$.[41,42] The non-equilibrium composition of the solid combustion products confers to them a relatively high chemical activity and a relatively low sintering temperature about 1470°C. Taking advantage of these features a wide range of Ti_3SiC_2-TiC_{1-x}-$TiSi_2$ materials could have been produced by adding of various amounts of silicon to the combustion products (Fig. 11). The materials obtained in this way form a group of ceramics with unique attributes showing a Young's modulus around 350 GPa, a low (Vickers) hardness between 2 and 6 GPa, a high fracture toughness (K_{IC} close to 10 MPam$^{1/2}$), a pseudo-plastic behaviour at room temperature and a plastic one at elevated temperatures coupled with a high chemical and corrosion resistance.

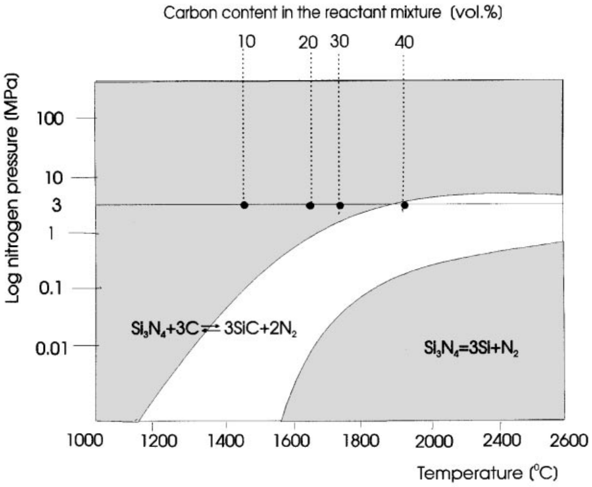

Fig. 10. Influence of temperature and nitrogen pressure upon the reduction of silicon nitride by carbon. On the diagram proposed in Ref. 33 have been inserted: (i) the content of carbon in the Si + C mixtures subjected to solid combustion under a nitrogen pressure of 3 MPa; (ii) by black points—the measured temperatures of solid combustion at given carbon contents in the reactant mixture (data after Ref. 13).

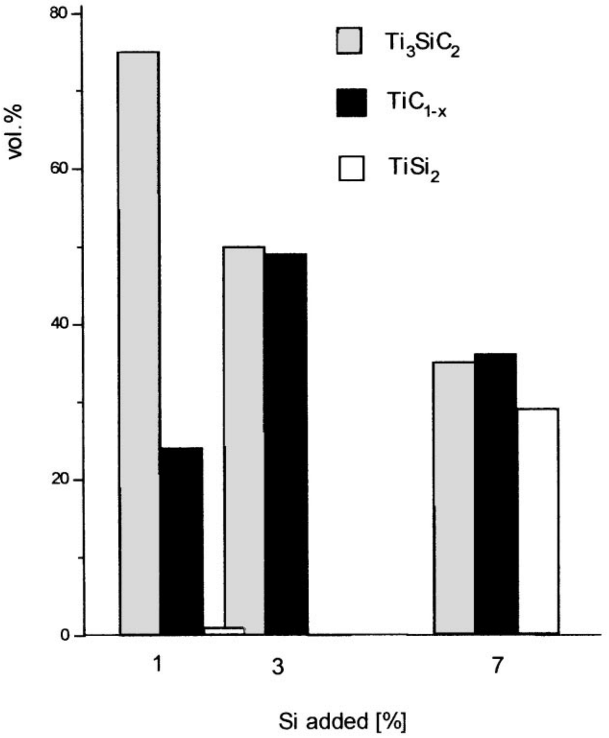

Fig. 11. Phase composition of materials produced by pressureless sintering at 1470°C of solid combustion-derived Ti_3SiC_2-based powders with various additions of Si (after Ref. 42).

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