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Stuijts Memorial Lecture 1997: Ceramic Science and Technology Facing Changing Paradigms

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Abstract

In the foreseeable future the main matter of concern for applied research into ceramic materials will be, on the one hand, the need to ensure the sustainable development by a reduction in the consumption of nonrenewable energy and natural resources and, on the other, the challenge associated with the tendency of the industry to move towards a sales-orientated and 'just-in-time' production of materials. The former concern should foster a growing utilisation of ceramic materials because these are, to an overwhelming majority, constituted by light elements that are abundant in the earth's crust and air. This endeavour emphasises a perfectioning of existing ceramic systems and their tailoring to a host of advanced applications by improving the properties, by using new or improved technologies, and by 'discovering' new properties of known compounds. This trend is illustrated in the paper by considering the applications of successively developed types of SiC-based materials and by the perspectives opened by newly revealed properties of earlier known materials, like Ti_3SiC_2. In addition to providing improved properties, newly developed ceramic technologies comply to an increasing degree with requirements for sustainable development and for 'just-in-time' production. To illustrate this tendency, the RBAO (reaction bonded aluminium oxide) method and several variants of combustion methods are reviewed in the paper. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

At present paradigms are changing in all spheres of life; and science and technology should not and are not an exception. Therefore, it is tempting to assess the changing paradigms taking shape in ceramic science and technology which seems to be a next-to-impossible task. Already in 1919 the famous chemist W. Ostwald wrote, 'To-day the production of new science has attained gigantic dimensions while the conjoint development of its assimilation among all members of our society science has not been not a subject of serious and methodic considerations'.[1] At the time of Ostwald's writing the number of published papers about materials and their technology was around 6000 per year while at present it is now doubling within every 5 years and may now be many tens of thousands per year. Therefore, for want of more knowledge we are getting drowned in the information ocean.

Nevertheless, some emerging trends in ceramic materials research may be discerned. Although science cannot cease to regard the disinterested pursuit of knowledge as its primary duty, the greater part of research in materials science has nowadays an applied character if not one that is concentrated on development and improvement of marketable products. In this perspective it is most probable that in the foreseeable future the main matter of concern for research into ceramics shall be the problem of ensuring sustainable development[2,3] and the questions associated with changing producing practice in industry and, consequently, with the attitude to traditional research ways.[4] In order to contribute to sustainable development, materials research should look for and realise ways of reducing the consumption of nonrenewable energy sources and of natural resources in the production and utilization of materials (Fig. 1). The change in producing practice which has the greatest bearing on applied research is the tendency towards sales-orientated production and, therefore, the growing interest in versatile, rapid 'just-in-time' production methods, in other words in producing only what is going to be used immediately on the market.

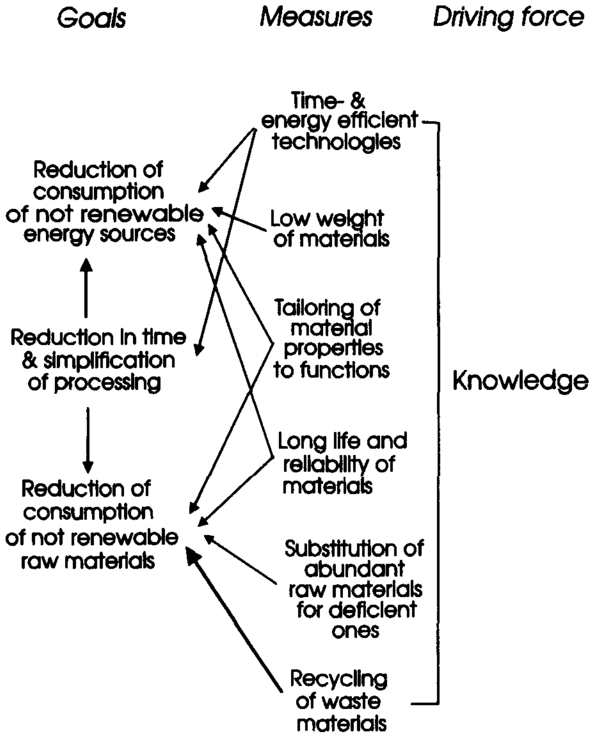


Fig. 1. Main goals and measures in material production which permit to establish sustainable development.

There is a growing body of published research which responds to these requirements and challenges. Some examples illustrating this tendency have been drawn subjectively from the field of experience of the author and are quoted in the present paper.

2 Reduction in the Consumption of Nonrenewable Natural Resources and Advance in the Implementation of Ceramic Materials

When the requirement for reduction in the consumption of nonrenewable natural resources is considered the need for further development and exploitation of ceramic materials is easy to understand because the overwhelming majority of ceramic materials are constituted by light elements such as silicon, aluminium, carbon, oxygen, and nitrogen that are abundant in the earth's crust and air (Fig. 2).[5]

Owing to their manifold properties, the ceramic materials, and especially the advanced types, have been already utilised to perform many functions. A further expansion in the use of ceramic materials may be realised in two ways. There is an enormous number of potential but still unknown compounds constituted by light elements because already the number of combinations $(C^n_r = n!/r!(n-r)!)$ among the $n = 12$ most abundant elements in the earth's crust taken, respectively, $r = 2$, 3, and 4 at a time is equal to 781. This number exceeds the number of known binary, ternary and quaternary refractory inorganic compounds, i.e. of ceramic compounds. Therefore, some authors speak of a yet unexplored 'mountain' of materials.[6]

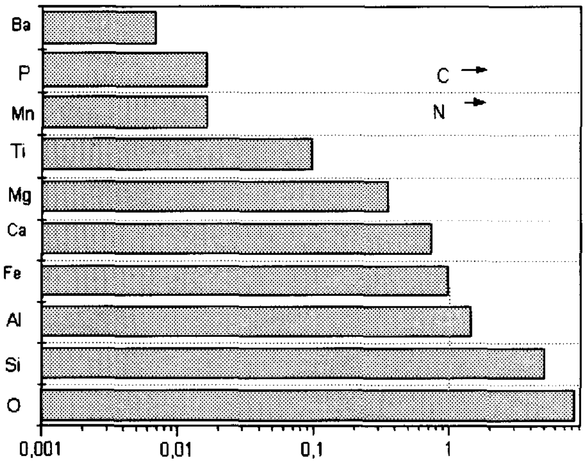


Fig. 2. Reserves of the most abundent elements in the earths crust (Na, K, and H excluded, fossil carbon and N_2 in air included). The reserves of iron taken as equal to one.

However, a search for new, yet unknown compounds seems not to be probable, and this in spite of the fact that advanced (special, fine) ceramics have appeared on the market later than metals and polymers and are, accordingly, less explored. In all historically proven stages of materials development[7] the longest spans of time were characterised by improvements of earlier known materials. Such a development is assumed to be taking place now with polymers[8] and seems to be being followed also by ceramics.

Therefore, one can expect that at present and in the foreseeable future the development of a broad palette of new ceramic materials for a host of high performance applications will take place predominantly on the basis of already known compounds and materials. This development can be realised by revealing new and/or not yet utilised properties, by improving fabrication methods or introducing new technologies, by varying the materials microstructure, and by combining various components. Such a way should be especially successful with ceramic compounds and materials because they have multifaceted properties. An example of such a development is provided by the large family of SiC-based materials which have appeared successively in response to emerging technical requirements (Table 1). Another well known example is furnished by ceramic composites (fibre-reinforced, particulate, nanocomposites) in which earlier known compounds are combined to produce materials having new properties. There has been spectacular progress with the known multicomponent oxides having the perovskite-structure and appreciated earlier for their dielectric properties. Owing to the discovery, by Bednorz and Mueller, that some oxides with this structure are superconductors at around 80 K they are now

Table 1. Utilisation of various properties of SiC-based materials in different applications

Property	*Application*
Hardness	Abrasive material
High thermal stability and strength at elevated temperatures	Refractories of universal applications in metallurgy and power industry (plates, retorts, recuperators, blast furnace linings, muffle kilns, etc.)
High resistance to irradiation and strength at elevated temperaturess	Fuel element cans in high-temperature nuclear reactors*
Electrical resistivity	Resistors, resistance heating elements
Semiconducting properties	Non-linear resistors, varistors, elements of wave-guides, ultraviolet receivers, cold cathodes, etc.
Resistance to acids and bases, abrasion resistance	Mechanical seals, bearings, nozzles
Elevated thermal conductivity, high thermal stability, corrosion and erosion resistance	Heat exchangers (tube and shell recuperators) in waste heat recovery and management
High strength and low weight of SiC whiskers, platelets and polycristalline fibres	Reinforcing components of composites
Pinning down of grain boundaries by nanometric (*n*) SiC particles	Ceramic matrix nanocomposites having a high creep resistance at elevated temperatures
Fracture characteristics under dynamic conditions	Bullet-proof vests, rocket parts, etc.

*Potential application.

regarded as the high temperature superconductors (HTC) par excellence.

Another example of the 'disclosure' of hitherto unknown properties of earlier known compounds is provided by the '312' and 'H' compounds. These compounds embrace among others Ti_3SiC_2, Ti_3GeC_2, Ti_2AlC, Ti_2AlN; they are nanolaminates in which the strength of the interplanar bonds is intermediate between that of the primary bonds and the interlayer bonds in graphite. Their structure and some of their properties have been known for many years[9–11] but only a successful synthesis of larger amounts, first by solid combustion[12–15] and then by arc melting and other techniques[16,17] permitted to produce polycrystalline materials and to measure further properties of these materials. According to the measurements, the materials show a set of properties not typical of any metallic, ceramic or polymeric material.[18,19] In fact the electrical, thermal and mechanical properties of these compounds are intermediate between typical metals and ceramics. In order to illustrate this the brittleness of Ti_3SiC_2 is compared in Fig. 3 with those of typical ceramic and metallic materials. The brittleness is expressed in terms of the brittleness parameter proposed in Ref. 20, namely: $B = H_{vc}\ E/K_{Ic}^2$ where: H_{vc} is the Vickers hardness measured at a transition point from load dependent to load independent values; E is the Young's modulus; and K_{Ic} is the critical stress intensity for mode I loading.

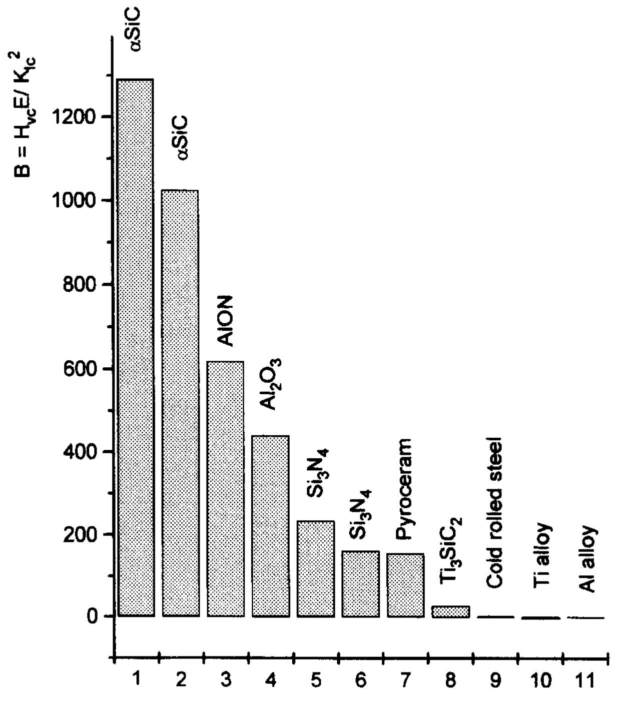


Fig. 3. The brittleness parameter, B, of some ceramic and metallic materials and of Ti_3SiC_2. Basic data used for calculation of B: for Ti_3SiC_2 after Refs 12, 14, 15, 17–19, for α SiC, AlON, Al_2O_3, Si_3N_4, after Ref. 20, for rolled structural steel, Ti alloy, and Al alloy according to various catalogue sources.

Of equal if not more interest is another unique property of Ti_3SiC_2, namely its easy machinability resembling that of wood and graphite.[18,19] Since machining constitutes an important part of fabrication costs for ceramics (Table 2), such a property should be of value under the conditions of a sustainable development.

Table 2. Distribution of production costs of a silicon nitride cam follower (after Ref. 21)

Stage of the technology	*Participation in the production costs (%)*
Powder synthesis and processing	35
Shaping, sintering and other operations leading to a densified material	17·5
Maching to final product	47·5

3 Energy-Saving and Versatile Nonconventional Routes to Ceramics

There is a growing body of published research, especially into nonconventional preparation routes for ceramics, which not only demonstrates improved properties in the products but also complies with the requirements of sustainable development by increasing energy efficiency and by responding to the requirements of 'just in time' production. Some illustrative examples of it are now quoted.

It is well known that reaction bonding (sintering) methods have a higher energy efficiency than typical sintering methods because of the partial utilisation of the heat of reaction for bonding and because of the ability to produce near-net shape components with reduced machining costs. Some of the reaction bonding methods are, in addition, versatile and, therefore, comply with the requirements of 'just-in-time' production. Such features are shown, for instance, by the RBAO method (reaction bonded aluminium oxide).[22–24] In this method, attrition-milled Al/Al_2O_3 powder compacts are heat treated in air such that Al oxidizes to form small 'new' Al_2O_3 particles which sinter and thereby bond together the originally added Al_2O_3 or other ceramic particles. By adding different starting components to the aluminium-bearing ones various alumina-based materials can be produced in a rather simple way. The 'Japanese tree' of this method, demonstrating its versatility, is shown in Fig. 4.[22]

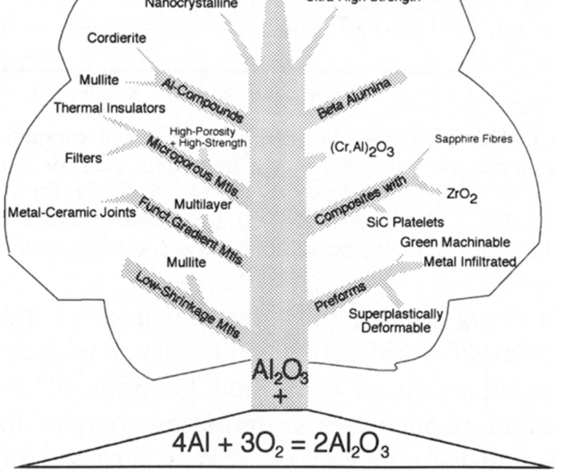


Fig. 4. The 'Japanese tree' of the RBAO (reaction bonded aluminium oxide) method; after Ref. 22.

Still more external energy is saved in the combustion methods for the synthesis of solids because here the energy derived from internal sources (heat of exothermic reactions) makes up a large part of the energy needed for the synthesis. Initiated by external heat sources, the exothermic reactions bring about an avalanche-like local temperature increase to high levels (ignition) and a self-sustaining propagation of the heat wave when a positive feedback is established in the reactive system. This occurs when the flux density of heat losses to the environment and colder parts of the system is less than the flux density of heat passing to the material next to react. In addition to the energy efficiency, many combustion methods feature additionally a high versatility which is desirable for the development of 'just-in-time' production methods. All these features of combustion methods can be illustrated with reference to the production of sinterable ceramic powders.

In the most developed method of combustion synthesis, namely solid combustion,[25–29] at least one of the reactants and the final products are solid and the production of heat occurs in the condensed state only. The method utilises exothermic reactions between elements (solid and gaseous), such as: $3Si(s,l) + 2N_2(g) = Si_3N_4(s)$ or $Si(s,l) + C(s) = SiC(s)$, thermite reactions or combinations of both, like: $3TiO_2 + 3C + (4 + x)Al = 3TiC + 2Al_2O_3 + xAl$.

The most known variant of solid combustion involves a layer-by-layer self heating to high temperatures by an interplay of the positive and negative feedback and is referred to as self-propagating high-temperature synthesis (SHS). The simple experimental arrangement used to put SHS in action is shown in Fig. 5.

Solid combustion has been most successful in the production of simple and composite nitride, carbide, and boride powders. It permits to access not only to the high temperatures needed for the synthesis of such compounds but also to high reaction rates. The latter are believed to be due, at least in Si- and Al- containing systems, to a 'migrating thin reaction layer' mechanism and to the precipitation of the final products from liquid solutions[30] (Fig. 6).

The occurence of this mechanism involving a liquid phase and others involving transport through the gas phase (Fig. 7) favours the formation of composite nitride, carbide, and boride powders which are characterised by a homogeneous distribution of the components. When sintering aids are required for densification of the

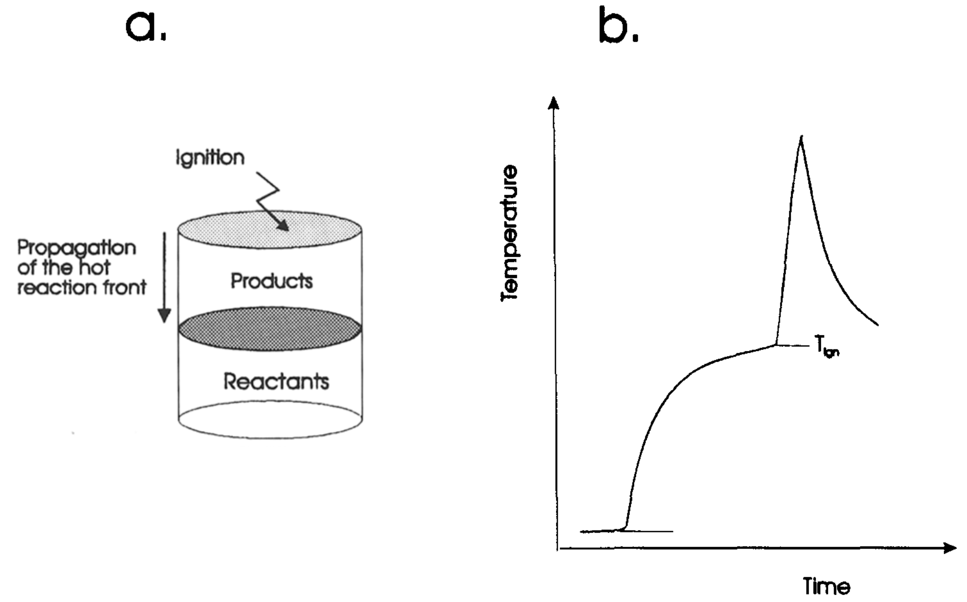


Fig. 5. Self-propagating high-temperature synthesis (SHS): (a) experimental arrangement; (b) temperature versus time at a given point of the reactive mixture.

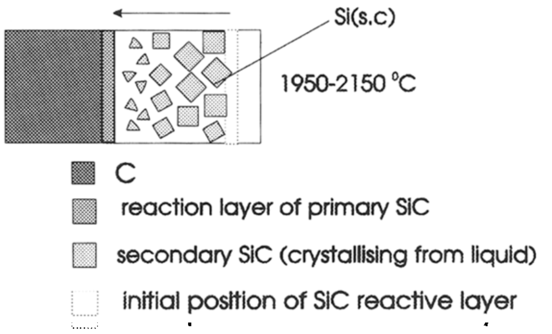


Fig. 6. The 'moving thin reaction layer' mechanism of reactions in the Si–C reactive system which occurs during solid combustion at 1950–2150°C. Due to similar rates of growth of SiC at the C–SiC interface and of dissolution of this primary SiC at the SiC/Si(1) interface a thin reaction SiC layer moves into C leaving in its wake supersaturated C solutions in liquid Si; precipitation of the final product (secondary SiC) occurs from the liquid phase; after Ref. 30.

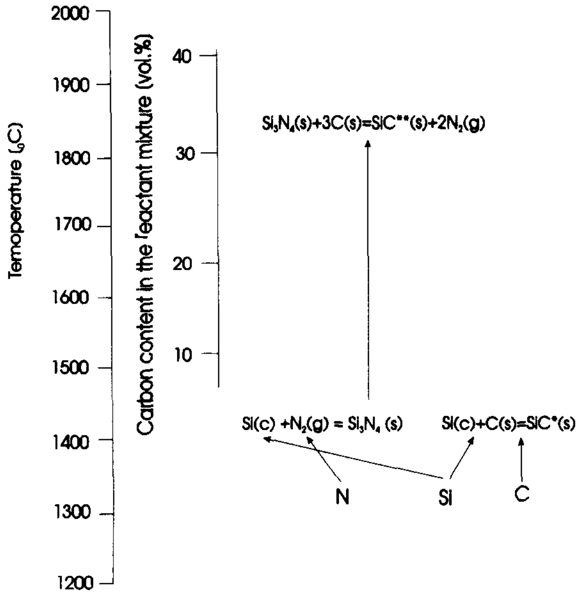


Fig. 7. Reactions in the Si–N–C system under conditions of solid combustion at different carbon contents in the reactant mixtures at the resulting temperatures of solid combustion; (after Kata, personal communication).

powders, their homogeneous distribution in the particulate product from the solid combustion is attained by adding the aids to the reactant mixture before the combustion synthesis (Fig. 8).

The features of the particulate products from solid combustion have allowed a simplification of their processing to yield sinterable powders in the case of SiC, Si_3N_4, AlN, composite SiC–Si_3N_4, SiC–B_4C, and Cr_2C_3 and a substantial reduction in the number of major processing steps of the in comparison with conventional methods.[31–33] This applies also to the synthesis of ferrites because of the absence of the first firing necessary in conventional methods; in solid combustion, ferritization already occurs in the course of the compound synthesis.[34] The extent of simplification which is feasible by using solid combustion is indicated by the flowsheets given in Figs 8 and 9 where a comparison is made between the production of sinterable SiC + B_4C and AlN powders by using, respectively, solid combustion and other advanced methods. Together with the extremely short time needed for the synthesis itself, all the above mentioned features render powder producing methods using solid combustion synthesis especially favourable for the development of 'just-in-time' production.

Solid combustion has also been found to be very successful in the production of powders of intermetallic compounds. To show but one example, the interaction of powders of Ti with Co or Ni during the synthesis of, respectively, TiCo and TiNi, by solid combustion is illustrated in Fig. 10.[35] The sequence of interactions resembles the one in the Al- and Si-containing ceramic systems, and involves consecutively: (partial) melting of one of the reactants with fragmentation of the more

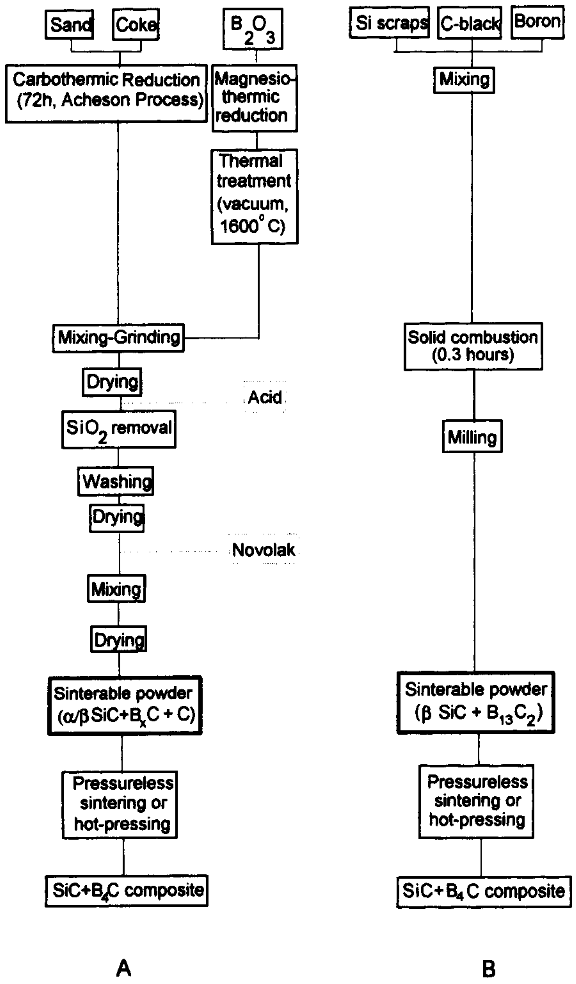


Fig. 8. Flow charts of production of sinterable SiC + B_4C powders by: (A) an advanced method utilising carbothermic and magnesiothermic reduction; (B) solid combustion.

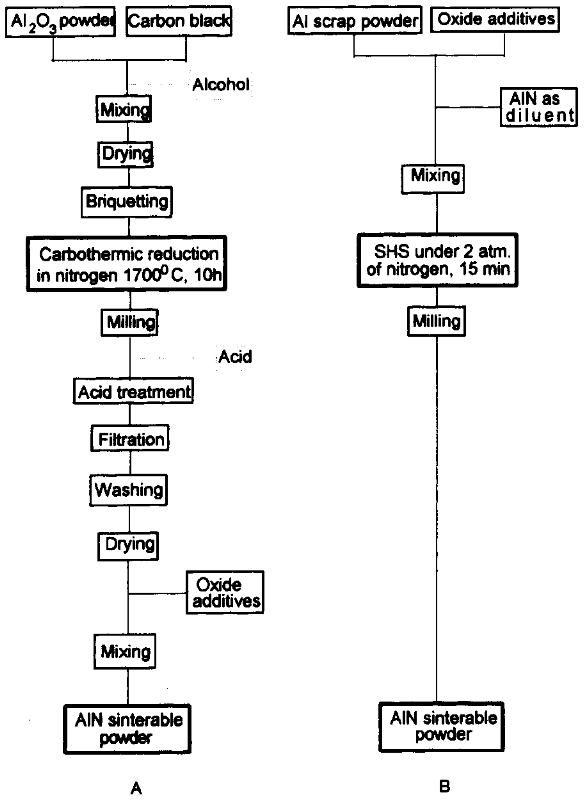


Fig. 9. Flow charts of production of sinterable AlN powders by: (A) carbothermic reduction; (B) solid combustion after Ref. 31.

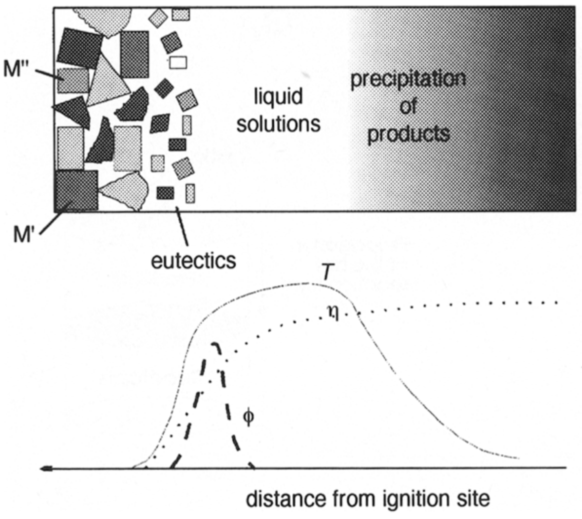


Fig. 10. Successive stages of interaction of titanium powders with nickel or cobalt on combustion synthesis of TiNi or TiCo. Legend: T, temperature; η, degree of advancement of the reaction; ϕ, heat production rate; after Ref. 35.

refractory one, formation of liquid solutions, and crystalisation of the final products from the melts. This facilitates the synthesis of intermetallics, especially from reactants with widely different melting points.

The value of other variants of combustion synthesis developed for the production of multicomponent oxide powders has also been demonstrated. When such oxide powders are prepared by solid state reaction of the components, they are often compositionally inhomogeneous and consist of hard agglomerates. Wet chemical methods developed to produce more homogeneous and fine powders are complicated and still require calcination to obtain crystalline products. However, crystalline multicomponent oxide powders may be prepared instantaneously by ignition and by self-sustaining combustion brought about by exothermic reactions in various redox mixtures such as citrate-nitrate gels[36,37] (Fig. 11), aqueous solutions of metal nitrates—urea (carbohydrazide)[38–41] (Fig. 12), and hydrocarbon aerosol sprays containing inorganic

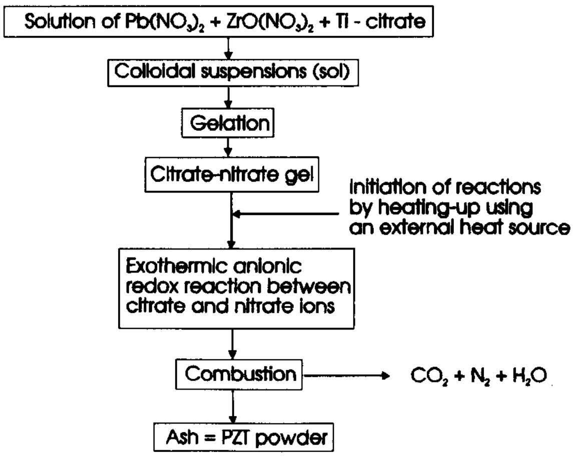


Fig. 11. Synthesis of PZT powders by self-sustaining combustion of citrate–nitrate gels; after Ref. 36.

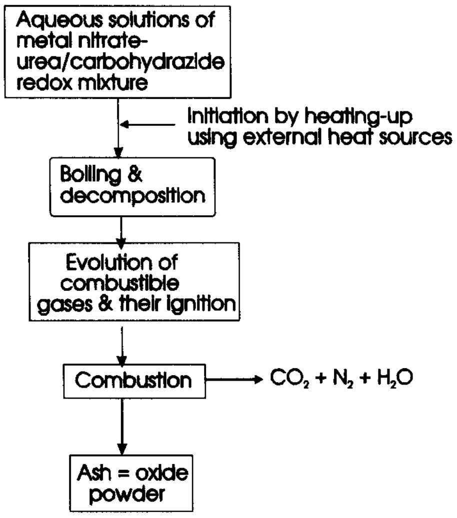
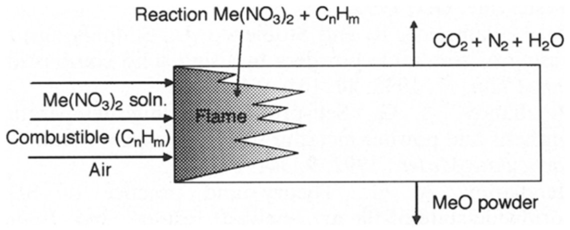


Fig. 12. Synthesis of composite oxides powders by combustion in combustible gases evolving from heated redox mixtures of aqueous solutions of metals nitrates and urea or carbohydrazide; after Ref. 38.

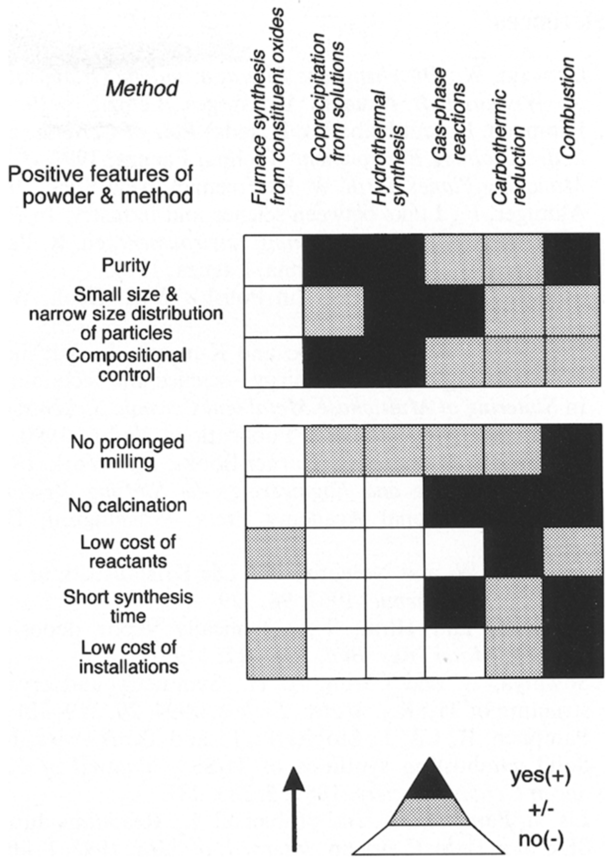


The reaction $Me(NO_3)_2 + C_nH_m = MeO + CO_2 + N_2 + H_2O$ produces most of the energy for pyrolysis

Fig. 13. Synthesis of oxide powders by self-sustaining pyrolysis-combustion of atomised redox mixtures of metal nitrate solutions (oxidiser) and hydrocarbons (fuel); after Ref. 42.

precursors of the oxides, usually in the form of metal nitrates (Fig. 13).[42] These methods have yielded homogeneous powders of: $Y_3Al_5O_{12}$, $tZrO_2/Al_2O_3$, MAl_2O_4, MCr_2O_4 (M = transition and alkaline earth metals), $La_{1-x}Sr_xMO_3$ (M = Cr, Mn, Co, and Fe), $YBa_2Cu_3O_x$, mullite, and other multicomponent oxides. The combustion-derived powders are characterised by fine particles ($< 1\ \mu m$) and by a narrow particle size distribution making the powders more sinterable than these obtained from other processing routes. All these variants of combustion synthesis are characterised by rapidity, simplicity, and versatility. The main features of the different variants of the combustion method and the main characteristics of the powders produced from this method are compared in Fig. 14 with the attributes of powders deriving from other advanced methods.

Combustion methods have also been expected to improve and/or simplify many other technologies but only some applications have turned out to be effective, such as metal-ceramic joining and the production of functional gradient materials (FGMs) where the rapid reaction rates can limit diffusional processes and maintain the compositional configuration of the starting body.[43] However, in the case of application of combustion for producing near-net shape materials in one step, combining combustion synthesis, shaping and densification, positive results have only been obtained with intermetallics and metal-ceramic composites;[34] ceramics have presented difficulties owing to their insufficient plasticity at elevated temperatures. An interesting application for combustion methods may arise in the CVD growth of diamond films because oriented diamond nuclei on substrates grow with higher rates and the resulting diamond films have a larger area uniformity when treated in a combustion system than when prepared by more conventional hot-filament or plasma CVD processes.[44]



Method / Positive features of powder & method	Furnace synthesis from constituent oxides	Coprecipitation from solutions	Hydrothermal synthesis	Gas-phase reactions	Carbothermic reduction	Combustion
Purity	no(-)	yes(+)	yes(+)	+/-	+/-	yes(+)
Small size & narrow size distribution of particles	no(-)	+/-	yes(+)	yes(+)	+/-	+/-
Compositional control	no(-)	yes(+)	yes(+)	+/-	+/-	+/-
No prolonged milling	no(-)	+/-	+/-	+/-	+/-	yes(+)
No calcination	no(-)	no(-)	no(-)	yes(+)	yes(+)	yes(+)
Low cost of reactants	+/-	no(-)	no(-)	no(-)	yes(+)	+/-
Short synthesis time	no(-)	no(-)	no(-)	yes(+)	+/-	yes(+)
Low cost of installations	+/-	no(-)	no(-)	no(-)	+/-	yes(+)

Fig. 14. Features of some powder producing methods and characteristics of powders from these methods.

4 Summary

Some examples have been presented to illustrate the changes of paradigm that are believed by the author to be taking shape in ceramic materials science and technology in response to the requirements of sustainable development (reduction in the consumption of nonrenewable energy and natural resources) and in response to the challenges associated with the trend in industry towards 'just-in-time' production.

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