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Review
Microstructural aspects of fabricating bodies by self-propagating synthesis

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Existing data on effects of reactant compact microstructure on self-propagating synthesis, SPS type reactions is reviewed. Propagation rates generally decrease with increased compact density at higher densities, and reactions are no longer ignitable at high densities. At lower densities the trends may vary depending on the reactions. Propagation rates and ignitability also generally decrease with increasing particle size, and can be affected by particle shape. More exothermic reactions lead to greater expansion, hence porosity, in unconstrained samples, while resultant pore sizes are effected mainly by outgassing. Final grain sizes are not a significant function of the initial particle size (but can be effected by finer residual porosity).

1. Introduction

Self-propagating synthesis (SPS), also referred to as self-propagating high-temperature synthesis (SHS), has attracted considerable attention, much of this for directly making bodies by igniting compacts of reactant particles by either general heating (allowing reaction to begin over a larger volume), or by a local, high temperature source. Local ignition typically results in a narrow, high temperature reaction zone which moves as a thermal wave through the material (commonly at velocities of a few mm s^{-1} to a few cm s^{-1}). Constraint or, especially, pressure may be applied in either of these cases, and is typically necessary to achieve relatively dense bodies. Much attention has been focussed on quite vigorous, and hence spectacular reactions, e.g., $Ti + C \rightarrow TiC$ and especially $Ti + 2B \rightarrow TiB_2$; much less attention has been given to microstructural aspects. These can have important inter-related effects via the: 1. reactant compact microstructures, i.e., particle sizes, shapes and contiguity, as well as the amount and sizes of intervening porosity effecting both mass and thermal transport in the compact, and the access and distribution of reactant or product fluid phases; 2. reaction front, e.g., apparently in the order of a few mm or less in thickness, which must interact with both the microstructural scale of the reactants and the resulting products; and 3. product microstructures, which must interact with the scale of the reaction front and the reactant microstructure. There are also possible interactions between macro- and micro-scale effects, including 1. the extent to which surface thermal losses, and thus specimen size and the surrounding media, effect reactions; and 2. possible bulk effects, e.g., expansion of unconstrained samples, as well as possible propagation direction effects. Thus, vertical propagation, i.e., top to bottom or *vice versa*, may be different from each other, and these in turn form horizontal propagation due to differing gravitational effects on expansion and on possible local melt flow, which is also likely to be effected by particle sizes via droplet sizes and capillarity. Also, if expansion can occur, then results can differ from unconstrained versus constrained specimens.

This paper reviews the microstructural aspects of SPS reactions combining the substantial Soviet, and the growing non-Soviet data, since the data is essential for understanding and controlling such reactions. Although microstructural characterization, e.g., due to fascination with the reactions themselves, is often limited as shown in Table I [1–6], there is sufficient data to show that microstructure can be quite important. This review is also presented to stimulate further attention to the microstructural aspects of these processes. Clearly, micro- and macro- aspects of these reactions cannot be entirely separated, so an effort will be made to note interrelations between them. Microstructural effects on ignition and propagation of these reactions will be reviewed first, followed by effects of reactant compact microstructures on reaction product microstructures.

2. Effect of reactant compact microstructure on reaction ignition, and propagation

2.1. Density and environmental effects

While only fragmentary microstructural information on reactant compacts has been given in many studies, more comprehensive studies [7–13] as well as other more limited results provide some general or specific insight into many of the above effects. Kudyashkin *et al.* [7, 8] generally showed distinct maxima in propagation rates for $Ti + 2B \rightarrow TiB_2$ at intermediate reactant compact densities, with the height and density for this decreasing with increasing particle size (Fig. 1), reaching ≈ 1 cm s^{-1} at $\approx 35\%$ density for 1650 μm diameter Ti particles. They also showed that

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TABLE I

Reaction		% Porosities		Particles/grains sizes (μm)		Reference
Formula	Conditions	Reactant compact	Reacted body	Reactant compact	Reacted body	
a) *$Si + C \rightarrow SiC$*						
Pressed pellets 6 mm diameter × 6–9 mm long. Conversion efficiency generally increased with decreasing particle size, and increasing pressure (to 3 GPa) and area (and/or possible direction) of ignition.		Not given (presumably $\approx$ 40–60)	$\approx$ 10	5 (Si) 10, 25 (C)	$\approx$ 5	Yamada *et al.* [1]
Pressed pellets $\approx$ 7 mm diameter and 25–30 mm long ignited by axial passage of current. Conversion efficiency.		Not given (presumably $\approx$ 30–50)	Not given (apparently still loosely consolidated)	5 (Si), 10 (C), 5 (Si), 0.03 (C) 0.01 (Si), 0.02 (C) 0.01 (Si), 0.03 (C)	No Ignition $\approx$ 1–10 $\approx$ 0.5–2 $\approx$ 0.1	Yamada *et al.* [2]
Pressed pellets ignited by inductive heating, $\approx$ 98% conversion.		$\approx$ 50	Not given (apparently still loosely consolidated)	$\approx$ 0.3 (Si) $\approx$ 0.025 (C)	$\approx$ 0.02–0.05[b]	Pampuch *et al.* [3]
Mixed Si powder + C fibres, incomplete reaction of fibres.		No densities or particle dimensions given.				Pampuch *et al* [4]
(*b*) *Nitrides*						
$3Ti + NaN_3 \rightarrow 3\,TiN + Na$ cold pressed pellets 2.5 cm diameter 2.5 cm long ignited at one end.		——No data given——		22 (Ti)	10	Holt and Kingman [5]
$3\,Si + 2N_2 \rightarrow Si_3N_4$ (with added $\approx$ 0.1 μm Si_3N_4). Powder packed in a porous cylinder 26 mm diameter, 30 mm long, ignited at one end under 3–50 MPa N_2.		60–85	Not given (apparently loose compact)	< 5 (Si)	Needle shaped grains $\leqslant$ 1 μm diameter with lengths 10–25 μm (with $\approx$ 20% Si_3N_4 addition and $\approx$ 2–5 μm with $\approx$ 40% Si_3N_4)	Hirao *et al.* [6]

[a] Mostly in agglomerates ($\approx$ 50 μm diameter).

[b] SiC generally in agglomerates that appear to be relics of the original C agglomerates.

ultrasonic activation of compacts increased the maximum propagation velocity and density (e.g. $\approx 300\ \mathrm{cm\,s^{-1}}$ and 150%, respectively,) at large particle sizes but only a limited amount (e.g. 10–20%) at fine particle sizes. Naiborodenko and Itin [8, 9] similarly showed a pronounced maxima for $Ni + Al \rightarrow NiAl$ of $\approx 9\ \mathrm{cm\,s^{-1}}$ at $\approx$ 35% density, and a limited maxima of $\approx 3\ \mathrm{cm\,s^{-1}}$ at $\approx$ 30% density for Co + Al.

Kirdyashkin *et al.* [7] showed a distinct maxima in propagation rates versus porosity of Ti + 2B compacts (Fig. 1). Rice *et al.* [11] (using lengthwise, horizontal propagation of rectangular plates $\approx 5 \times 2.5 \times 0.6$ cm, usually constrained in a graphite cavity $\approx$ 0.6 cm deep) showed similar maxima for several Ti-based reactions (Fig. 1). Ignition was not feasible at densities significantly higher or lower than for the lowest propagation velocities measured. That propagation truly ceases at high densities, rather than being an ignition problem, was shown by ignition in lower (e.g., 60%) density sections of Ti + C (or Ti + 2B), with propagation ceasing in denser (e.g., 90% dense) portions of sections having a density gradient [12]. This effect of density on ignition and propagation behaviour has been attributed to a balance between having enough particle contact to aid reaction but not too much to lead to excessive thermal loss from the reaction zone. Thus, by accounting for density effects, comparison of propagation rates as a function of other variables (e.g., adiabatic temperatures) becomes feasible or more accurate.

Three other experiments indicate some of the variability that can occur due to scale and surrounding effects in the above propagation trends [11, 12]. Limited experiments with unconstrained plates (setting on top of the graphite holder, instead of recessed in it), showed similar propagation rates for Ti + C bodies which exhibited limited or no expansion on reaction. Thus, limited, or no effect of thermal conductivity of the graphite holder was indicated. However, significantly higher (e.g., $\approx 3\ \mathrm{cm\,s^{-1}}$ compared with $\approx 1\ \mathrm{cm\,s^{-1}}$) propagation rates were observed for $Ti + C \rightarrow TiC + 20$ v/o Ti compacts cold rolled in a steel, insulated, (flattened) tube of similar dimensions as the above plates (about half the thickness). Conversely, use of a single tow of graphite fibre infiltrated with Ti powder (to give $\approx$ TiC + 15 v/o Ti) propagated at similar rates ($\approx 0.8\ \mathrm{cm\,s^{-1}}$) when surrounded by air but dropped progressively to $0.69\ \mathrm{cm\,s^{-1}}$, $0.63\ \mathrm{cm\,s^{-1}}$, and then no propagation when resting, respectively, on a porous Al_2O_3, dense Al_2O_3 and graphite bricks, showing limited effects of small lateral dimensions, but marked changes due to surrounding thermal conductivity. Borovenskaya *et al.* [10] show-

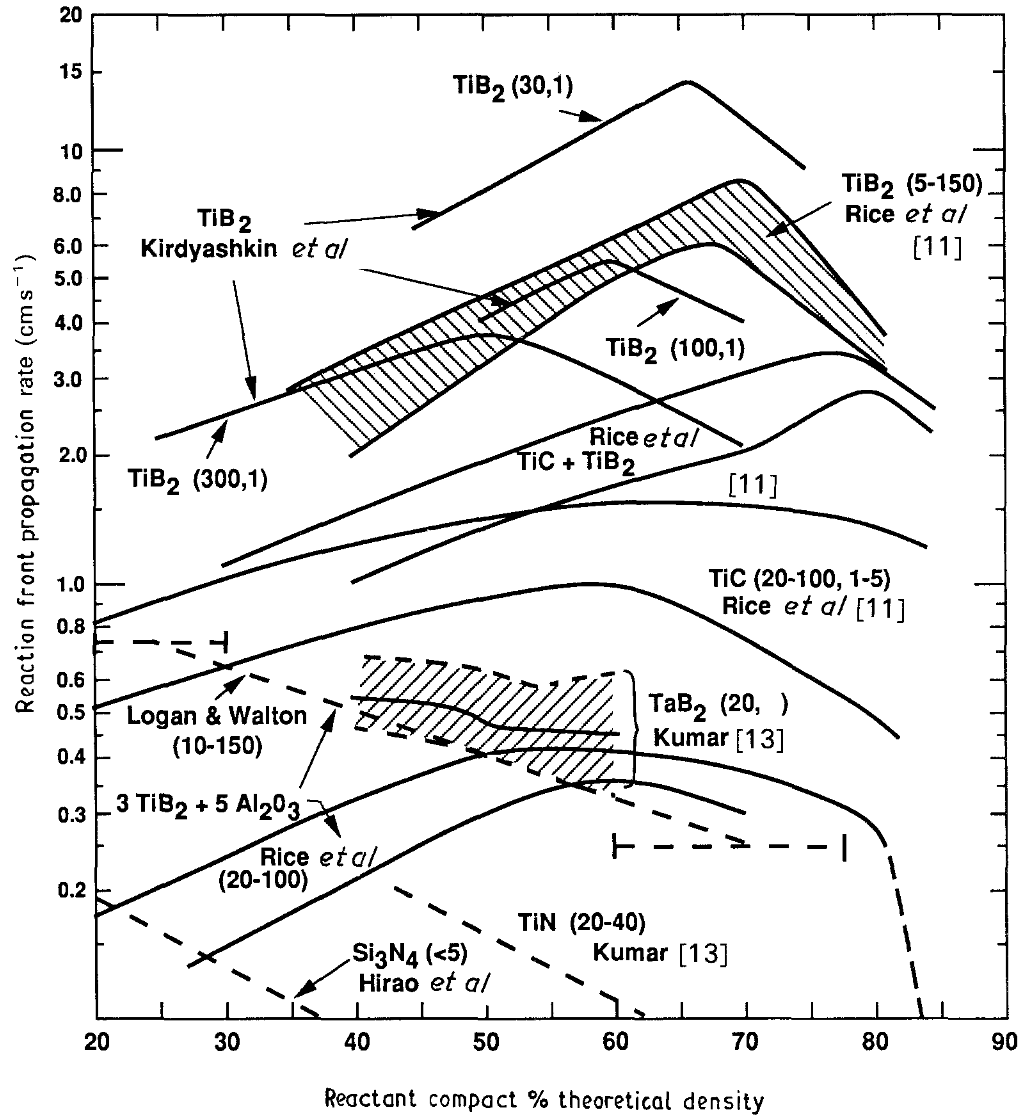

Figure 1 Reaction propagation rate versus theoretical density of reactant compacts. Figures in brackets are the particle sizes (in μm) of reactant particles with the cation listed first and the anion listed second (separated by a comma). The solid line shows Kumar's as-measured TiB_2 data; the upper and lower dashed lines show the possible range of corrections due to affects of expansion of his compacts on true propagation velocities.

ed propagation velocities for forming ZrB_2 increasing about 50% as the specimen diameter increased from ≈ 0.5 to ≈ 1 cm, which then remained constant. Kumar [13] also showed effects of surrounding thermal conductivity, e.g., about 10% higher propagation rates for insulated compared with non-insulated specimens. He has also shown lower velocities, e.g., by two or more, in $MoSi_2$ specimens, a little over 1 cm diameter against specimens ~ 2 cm diameter Naiborodenko and Itin [9] similarly showed propagation rates increasing by $\approx 25\%$ as the diameter of compacts to produce NiAl increased from ≈ 0.5 to ≈ 2 cm.

Logan and Walton [14] reported ignition and propagation of $3TiO_2 + 3B_2O_3 + 10Al$ mixtures, and of pairs of these reactants as loose powder or pressed pellets (apparently 0.5–0.75 of the theoretical density, held in SiO_2 crucibles) ignited by either 1. a nichrome wire (usually on top for downward propagation but some trials, with ignition at the bottom, apparently gave similar results) or 2. placing them in a heated furnace (monitoring the ignition temperature via a thermal couple). Overall, samples with finer (≈ 25 μm) Al particles ignited more readily than coarser ones (≈ 90 μm). While there may have been some tendency for easier ignition with finer TiO_2 or B_2O_3 ($-100/+200$ and -300 mesh), this is not clear. Except for the $3TiO_2 + 4Al$ reaction, the other two component reactions seemed more ignitable using the nichrome wire on pressed pellets than loose powder. Furnace ignition was easier (i.e., occurred at lower temperatures) for loose powder compared to pressed pellets. (Possibly due to faster interior heating via hot air permeation?) Ignited loose powder samples of $3TiO_2 + 4Al$ propagated at ≈ 0.4 mm s^{-1}, a pressed pellet of $B_2O_3 + 2Al$ at ≈ 1 mm s^{-1}, and loose powder and pressed pellets of $3TiO_2 + 3B_2O_3 + 10Al$ at ≈ 7.5 and ~ 2.4 mm s^{-1}, respectively. The former rate for loose powder is clearly higher, while the rate for the pressed pellet appears to be consistent with the results of Rice *et al.* [11] (based on the pellets of this composition being $\approx 2/3$ of the theoretical density, Fig. 1). The higher rate for the loose powder may reflect shrinkage effects or possibly greater insulation effects of the SiO_2 holder for the powders.

Propagation rates for $Ti + 2B \rightarrow TiB_2$ of ≤ 2 cm s^{-1}, and 4–6 cm s^{-1} have been reported, respectively, by Holt *et al.* [15] and Azatyan *et al.* [16]. The latter agrees reasonably well with Rice *et al.* data

(Fig. 1), assuming Azatyan *et al.* did not have a particularly high or low reactant compact density. In view of the results of Holt *et al.* indicating an $\approx 60\%$ of theoretical density, their values are low relative to those of Rice *et al.*, due mostly, if not completely, to the dilution effects with TiB_2 (discussed later, see also Fig. 3). Yamada *et al.* [2] report that cold pressed bodies (densities not given) of 5 μm Si and 10 μm C were not ignitable to give SiC but that 5 μm or 0.01 μm Si were ignitable with 0.2 or 0.003 μm C. Increasing the size of the Ti particles reacting with Si has been reported to change the mode of propagation from a stable, uniformly propagating reaction from an unstable spin mode [16].

Kumar [13] has recently reported propagation rates for the reaction $Ta + 2B \rightarrow TaB_2$ as a function of density using cylindrical specimens of 1.27 cm diameter and 3 cm long, propagated vertically (apparently no difference for propagation top to bottom or *vice versa*). His velocities show a limited decrease (0.55 to 0.45 $cm\,s^{-1}$) over his limited (≈ 40–60%) porosity range (Fig. 1). However, both this limited range and the complications of unconstrained specimens, with a resultant expansion from 23 to 37% in length as density increased, question his claim that his data is inconsistent with a maxima in propagation rate as a function of density.

Hirao *et al.* [6] report propagation rates for SPS of Si_3N_4 from Si and N_2 dropping from $\approx 2\,mm\,s^{-1}$ to $\approx 0.8\,mm\,s^{-1}$ as compact theoretical density increased from ≈ 18 to $\approx 40\%$. The low level of these propagation rates is generally consistent with the lower heat of reaction. Kumar [13] reports similar effects for solid particle–gas reactions, e.g., propagation of the $Ta + N \rightarrow TaN$ reaction increasing from 0.056 $cm\,s^{-1}$ at 1 bar N_2 to 1.6 $cm\,s^{-1}$ at 35 bars of N_2 pressure (average specimen $\approx 40\%$ of the theoretical density). Similarly, he reports propagation of $Ti + N \rightarrow TiN$ decreasing from 0.2 to 0.08 $cm\,s^{-1}$ at density increases from 43 to 67% of theoretical, and from 0.19 to 0.12 $cm\,s^{-1}$ as the Ti particle size increased from 1–5 μm to the order of 200 μm (at $37 \pm 4\%$ of the theoretical density). These trends for increasing propagation rates at such low compact densities are not consistent with most trends of Fig. 1 for all condensed phase reactants. This difference is attributed to the increasing density of the metal compacts restricting the access of the reactant gas, N_2. The volume of N_2 needed for nitridation is much greater than that of the compacts, even at the N_2 pressures used (e.g., to 15 MPa for Hirao *et al.* [6]) thus requiring N_2 access into the specimen for full reaction. Hirao *et al.*'s fine Si particle size (< 5 μm, and the finer size ≈ 0.1 μm, of up to $\approx 20\%$ Si_3N_4 added) would be particularly restrictive. Increasing propagation rates from ≈ 0.6 to $\approx 1.8\,mm\,s^{-1}$ as the N_2 pressure increased from ≈ 3 to ≈ 15 MPa, supports this.

2.2. Particle size and shape, and dilution effects

Several investigations [7–9, 11, 13, 17] show propagation rates clearly increasing with decreasing particle size (e.g. Fig. 2). While some studies [8, 9] indicate propagation rates continuing to rise with particle size decreasing over the entire range studied, others (e.g., [8, 18] for TiC, Borovenskaya *et al.* [10] for TiB_2 [17]) show such increases ceasing at finer particle sizes, e.g. < 50 μm. Similar limiting effects at finer particle size are also indicated in forming NiAl [8, 9]. Kumar [13] reports a small increase in propagation rate as Ti particle sizes increased from ≈ 2 to ≈ 90 μm in the $Ti + C \rightarrow TiC$ reaction. However, the combination of his data with that of Rice *et al.* [11] suggests an overall decrease in propagation rate with increased particle size, generally consistent with that of Kirdyashkin *et al.* [7, 8] over most of the particle size range but with little or no decrease at smaller particle size.

Rice *et al.* [11] also showed effects of reactant physical character, e.g., Ti or C as foil sheets or flakes of these, prevented ignition. Additionally, reactant compacts consisting of only large (e.g., 220 μm diameter) Ti spheres and finer C powder would not ignite, while compacts consisting of compacts in which $\approx 40\%$ of the Ti had such spheres (the remainder being -325 mesh particles) ignited, but propagated slower (1.30 $cm\,s^{-1}$) than when all the Ti was -325 mesh (1.55 $cm\,s^{-1}$). On the other hand, use of the same Ti spheres by themselves or mixed with finer Ti particles to react with B to form TiB_2 resulted in ignition and reaction in both cases with no residual Ti spheres left.

Composition, of course, plays an important role in ignition and propagation, i.e., ignition not being feasible unless reactions are sufficiently exothermic, and propagation rates generally increasing with reaction energy release. However, composition is also a factor from the standpoint of dilution of the reaction by either adding end product particles to reactants, excess of a reactant, or some inert filler. Thus Borovenskaya *et al.* [8, 10] showed substantial decreases in propagation velocity for elemental reactions producing HfB_2, TiB_2, or ZrB_2, each diluted with their own products (Fig. 3). The data of Holt *et al.* [15] for limited experiments in adding excess TiB_2 to reactants to form $TiB_{1.5}$ or TiB_2, showed considerable reduction in propagation rates. Extrapolation of these rates to no TiB_2 addition gives propagation rates consistent with those of Azatyan *et al.* [16] and Rice *et al.* [11] (e.g., Fig. 1, at $\approx 60\%$ of the theoretical density as used by Holt *et al.* [15]). Novikov *et al.* [8, 19] show similar dilution effects for Ti and other borides. More extensively, Kumar [13] showed effects of additions of product particles to reactions producing TaB_2 and $MoSi_2$ as well as effects of excess C in TiC (Fig. 3). He also showed a marked maximum as the molar ratio of B to Ta rises from 50 to 100%, then decreasing less severely as this increases to 250% (e.g., $TaB + 2B$ and $TaB + \alpha Ta$ plots in Fig. 3). While his velocities are most likely again effected by the substantial elongation of his specimens (e.g., 18–60% for the Ta–B), overall, his results are consistent with those of Holt *et al.* [15]. It is also expected that dilution of TiC with 10–30 v/o Ti by Rice *et al.* [11] is a reason for the broader range of their propagation rate data (Fig. 1).

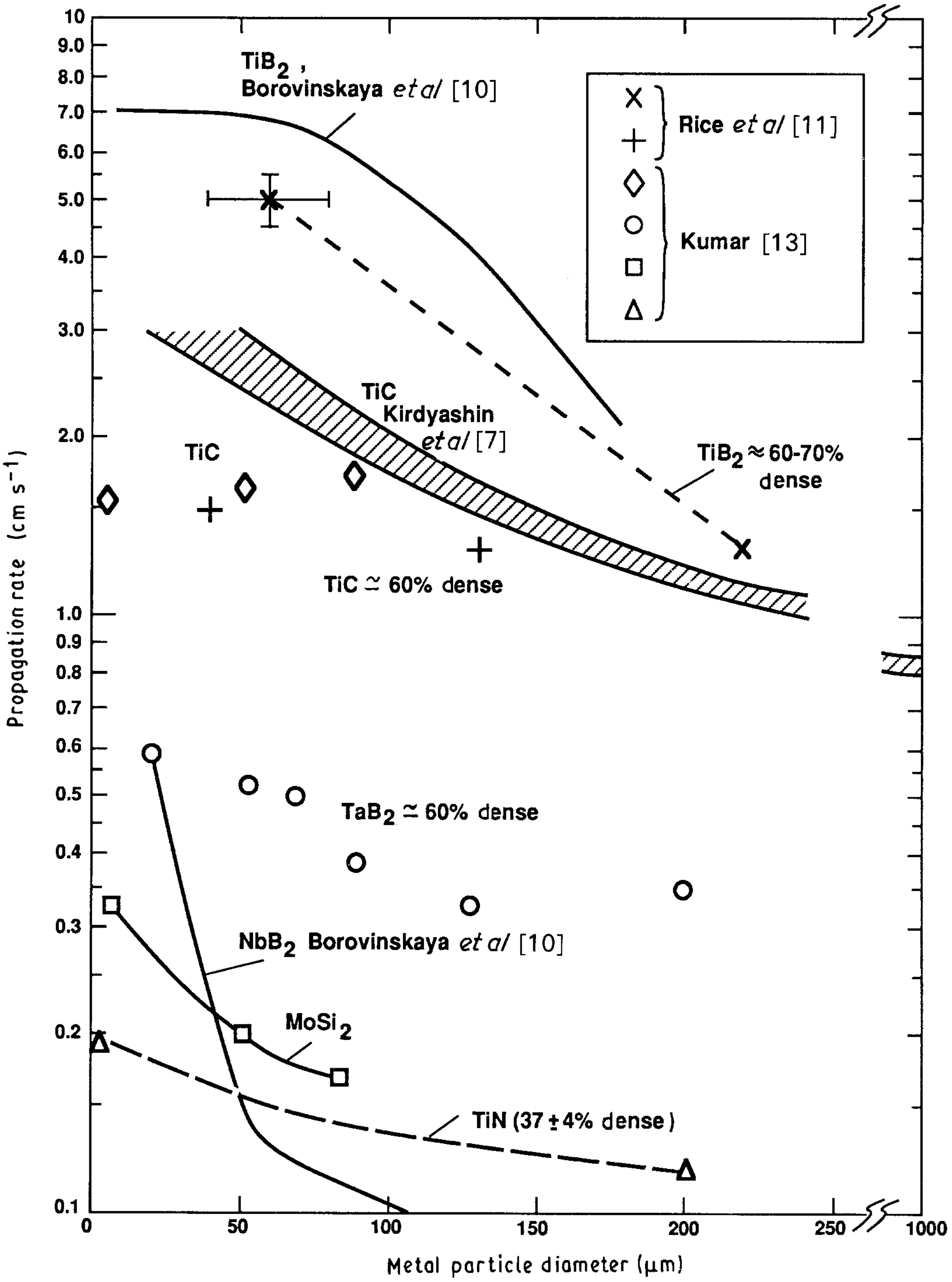

Figure 2 Reaction propagation rate versus metal particle diameter. Note the general agreement between data of Rice *et al.* [11] and Kumar [13] for TiC obtained from Ti particles of the order of 40 μm in diameter and of Rice *et al.* [11] and Kirdyashkin *et al.* [7] at larger particle sizes. In Rice *et al.*, the TiC point plotted for a Ti particle diameter of 130 μm reflects data for a body consisting of approximately 50% of 40 μm Ti particles and the remaining 220 μm Ti particles, which generally did not react [11]. Using only 220 μm Ti particles, the TiC reaction was not ignitable as discussed in the text. Also note the approximate agreement of TiB$_2$ data of Rice *et al.* [11] and Borovinskaya *et al.* [10].

Again similar dilution effects have been shown in producing NiAl [8, 20].

3. Effect of reactant compact microstructure on the reaction product character

3.1. Effects on composition and porosity

Reactant particle character can effect the reaction products. Thus, the earlier noted use of large Ti spheres in combination with finer Ti powder in reactions to produce TiC left the spheres unreacted [11] and, hence, also left some residual carbon content. Similarly, Yamada *et al.* [1] reported that the efficiency of reacting Si and C to produce SiC increased from ≈ 99% to 100% with decreasing particle size of ignitable composites in their work noted above. More specifically, earlier work by Azatyan *et al.* [16] has shown that products of reaction between Ti and Si shifted from Ti_5Si_3 to $TiSi_2 + Ti$ as the titanium particle size increased from less than 100 μm to more than 100 μm. These observations suggest that the incomplete reactions are related to the absence of, or incomplete, melting of larger particles despite the fact that expected, and in some cases, measured reaction temperatures, (i.e., on a macro-scale) are above the melting temperatures of the particular particle.

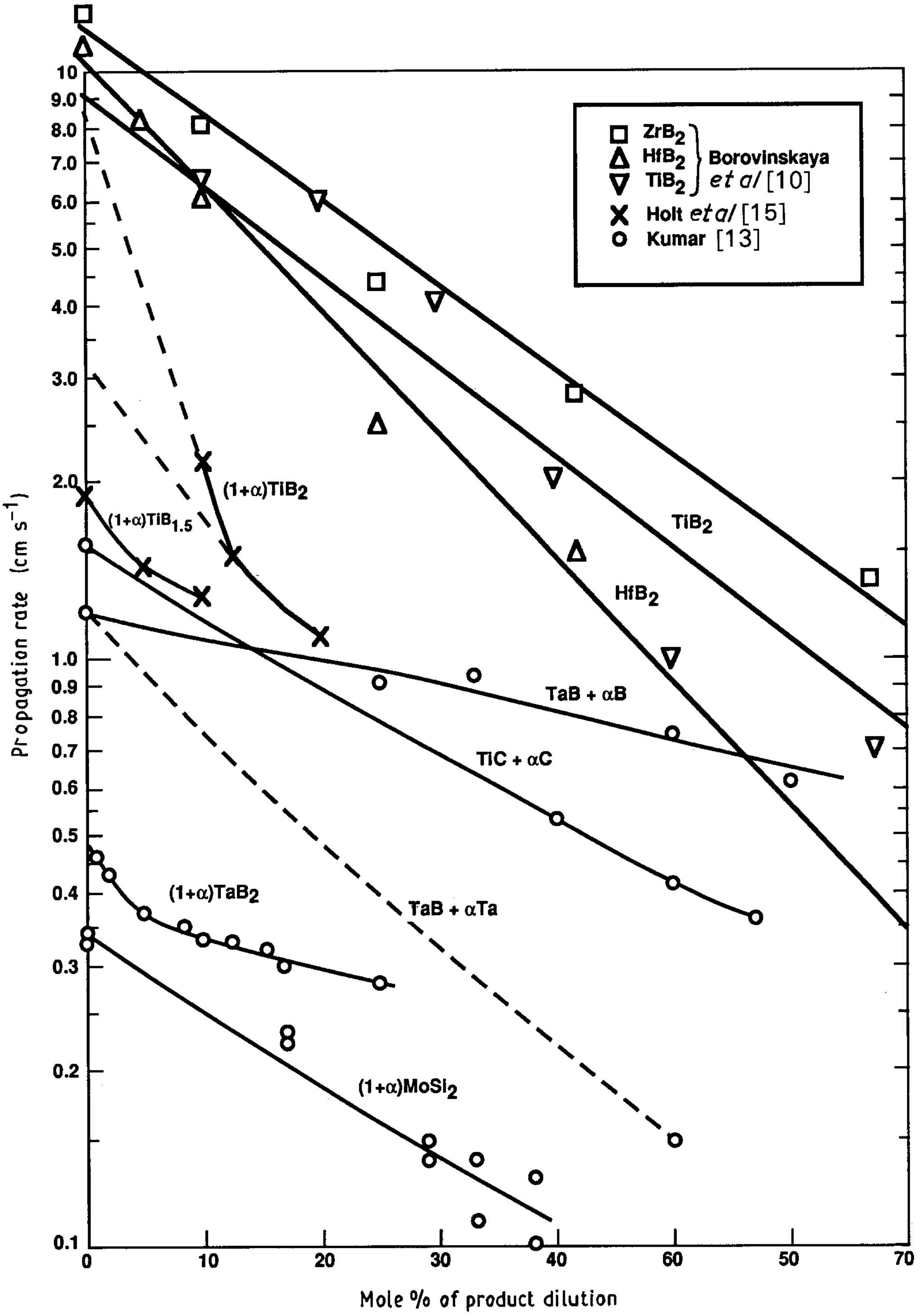

Figure 3 Propagation rate versus mol. % of product used to dilute the reactant compact. Note the significant reduction in propagation rate with increased dilution. Also that extrapolation of Holt's *et al.* [15] data for TiB_2 to zero dilution yields propagation rates generally consistent with other investigators (as shown in Fig. 1).

As a potentially important extension of this particle size effect, Rice suggested coating one reactant onto particles of another reactant [21], e.g., to aid understanding the reaction process as well as control the nature of reaction products involving three or more constituents. Thus, it has been suggested that coating B and Ti particles with C, could significantly change the nature of the resultant products, presumably giving significant B_4C with sufficiently thick C coating than from simple mixtures of Ti, B and C particles (giving mainly TiB_2 + TiC). Such coatings might also reduce outgassing problems, e.g., by outgassing more reactive particles while coating them with reactants that are less reactive with gaseous environments, as well as by increasing particles sizes, hence reducing the net surface area. However, to date, apparently no such experiments have been performed.

Turning to more specific aspects of effects on porosity Rice *et al.* [11] and Kumar [13] showed higher expansions (i.e., higher final porosity) for more exothermic reactions for unconstrained specimens (Table II). Kumar showed the extent of expansion generally increases as the density of the reactant compact increases (Fig. 4). Rice *et al.* [11] showed that finer reactant particles tend to give higher expansions. Kumar [13] also showed a decrease in expansion in

TABLE II Expansion of reactant compacts of different SPS reactions

Reaction	ΔH (J mol^{-1})	Adiabatic Temp. (K)	Linear Expansion ($\Delta l/l_0$, %)
$Ti + 2B \rightarrow TiB_2$	279 890	3 200	50–100%
$Ta + 2B \rightarrow TaB_2$	209 500	2 700	23–37% 42–60%
$Ti + C \rightarrow TiC$	184 900	3 200	0–20%
$Mo + 2Si \rightarrow MoSi_2$	131 570	1 900	0–6%

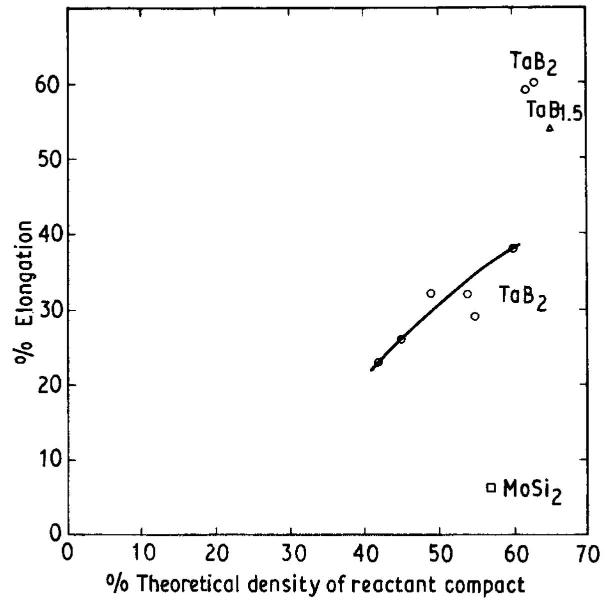

Figure 4 Percentage elongation of unconstrained reactant compacts as a function of the percentage of theoretical density for data on compacts after Kumar [13]. Note the difference in data for TaB_2 from two different sets of experiments; one deals with the effect of density on propagation in stoichiometric TaB_2, and one (the upper set of data) with the effects of stoichiometry on propagation rates.

the $MoSi_2$ reaction as the initial temperature of the reactants increased, e.g., from 6.4% at room temperature to 0% at 715 K. For reactant compacts that are constrained during the reaction, there should be fairly direct correlation between the starting and finishing amount of porosity. Again, however, one has to take into account the issue of intrinsic porosity generated due to the intrinsic volume decreases associated with the reaction [22].

The size of the resultant porosity appears to be significantly impacted by outgassing and consolidation conditions. Thus, unconstrained reactions can have larger pores due to expansion during reaction whereas constrained reactant compacts have smaller pores and consolidated bodies even smaller pores [23]. Clearly, a complicating factor is the formation of liquid phases which may significantly change the pore structure. However, Riley and Niiler [24] report that pores in material between larger pores from outgassing show a one-to-one correlation with the particle size distribution of Ti particles in forming TiC in constrained reaction compacts. They attribute this to the formation of molten Ti reacting with the C particles, thus leaving voids where the original Ti particles are located.

3.2. Effects on grain structure

There are clearly limitations on the effect of the starting particle size of the reactants on the resultant product grain sizes since there must be significant interdiffusion of constituents from different reactant particles in order to form the product. This relationship is probably further limited whenever liquid phases are formed during the reaction. One study [23] shows resultant TiC grain sizes from reacting Ti and C in the range of approximately 5 to 20 μm over a considerable range of reactant particle sizes, character, density and reaction conditions, with much of the grain size variation attributed to simple statistical variations. The starting compact porosity does not appear to effect product grain size much, because much of the resultant porosity is fairly substantial in size, presumably due to outgassing, leaving most of the grain structure occcurring in the relatively dense webs between pores. However, where pores which are less than the grain size are trapped in the webs, reduced grain sizes are observed. No clear trends were found with the amount of excess Ti (from 10 to 30 vol %), on whether the starting Ti was a foil or particles of different sizes, or whether the processing was simple ignition and propagation in air or ignition under pressure for hot pressing. At least two other studies [25, 26] are known to have resulted in TiC grain sizes of ≈ 20 μm, again indicating limited effects of starting particle size on resultant grain size. Yamada *et al.* [2] report fine Si (0.01 μm) and C (0.21 μm) particles gave fine (e.g., $\approx 0.2 \leq$ μm) SiC crystallites, while use of coarser Si (≈ 5 μm) gave SiC particles/crystallites of ≈ 10 μm in size; (use of 10 μm C particles was tried only with the larger Si particles, leading to no ignition as noted earlier). Whether this is due to the C particles limiting molten Si consolidation by capillary effects, is unknown.

A remaining important microstructural issue is whether reaction processing can or does result in any other different microstructural characteristics such as contiguity than would be simply obtained from processing similar composites by simply mixing the ingredients. While no stereological studies are known to have been performed to date, overall, similar strength, elastic and especially, electrical properties of composites consisting of $Al_2O_3 + TiC$ or $Al_2O_3 + TiB_2$ made by either route, suggest no generic differences in contiguity of reaction processed composites from those made by simply mixing the product ingredients [27].

There have been indications that *in-situ* whisker formation can occur in SPS formed bodies, however, some of these observations have been found not to be true whiskers [23]. Thus, predominantly Ti-containing fibrous features in these bodies were found to be "growing" out of a space between grains at the bottom of a pore or on a fracture, though often found bent, twisted or both. They were concluded to be the result of molten, or near molten, Ti that was extruded out between grains (probably mainly TiC but possibly some C grains), and may or may not have subsequently reacted. They are thus clearly not whiskers. However, whisker-like features seen in Al_2O_3–TiB_2

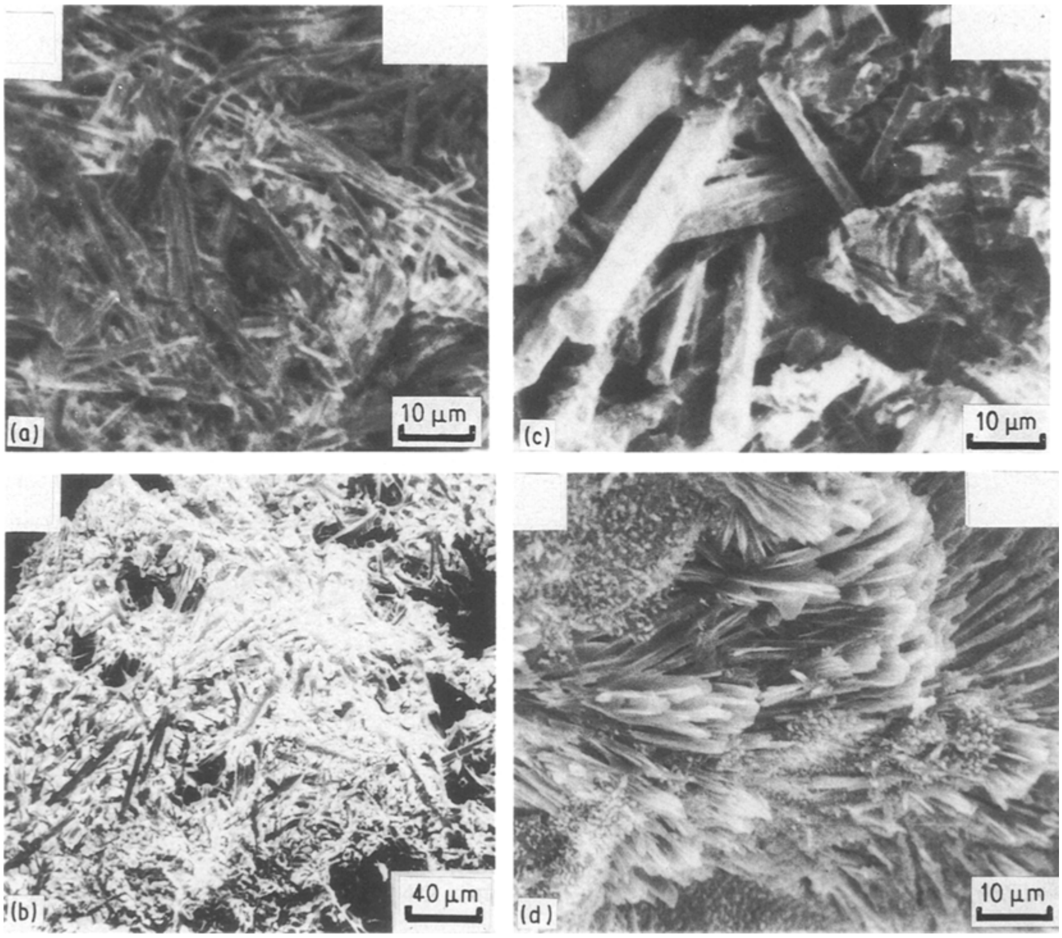

Figure 5 Examples of whiskers or whisker-like grains in $5Al_2O_3$–TiB_2 composites produced by reaction of Al, TiO_2 and B_2O_3. (a)–(c) are from hot rolling experiments at NRL. (d) is from hot pressing experiments at W. R. Grace (photo courtesy of Dr. J. H. Enloe). The chemical species of the whiskers have not been identified. (K. C. Logan's suggestion in a private communication in 1989, that these may be aluminium borate whiskers, however, seems logical.)

bodies (e.g., Fig. 5) appear to be true whiskers. Some of these similarly appear to be the result of extrusion processes but some simply appear to be lying on the surface of the pores. Thus, *in-situ* whisker formation in SPS reactions appears to be at best a sporadic process of very limited occurrence.

Finally, consider the issue of the scale of the mixing of the reactants on the homogeneity of the resultant product. While one might presume that reaction processing could reduce the requirements for uniformity of mixing because of the mixing that results from the reaction itself, especially where liquid phases are formed, there still is the important issue of the degree of homogeneity that is required. Limited work has demonstrated that inhomogeneities in the reactant compact clearly can lead to inhomogeneities in the resultant product. Thus, in the reaction of Al, C and TiO_2 to form $Al_2O_3 + TiC$, laminar graphite defects have been found scattered throughout the bodies, with the more serious of these frequently found to be fracture origins and, hence, strength limiting [27]. Similarly, heterogeneous Al_2O_3 grain sizes in $Al_2O_3 + TiB_2$ composites from reaction hot pressing of Al, $B_2O_3 + TiO_2$ suggest effects of mixing inhomogeneities.

4. Summary and conclusions

Reactant compact density has a major effect on SPS ignition and propagation. A variety of reactions show propagation rates decreasing with increasing density (decreasing porosity) at higher densities and generally not being ignitable at high densities. At lower densities, two different trends are seen, apparently depending on the nature of the reactants. Limited data for reactions in which one reactant is a gas, show propagation rates continuing to increase with decreasing density. On the other hand, considerable data for reactions in which all (initially) solid reactants show propagation rates decreasing with decreasing densities at lower densities. These reactions thus generally show a pronounced maxima in propagation rates, e.g., at 50–60% of theoretical density, with propagation, and hence also ignition, below $\approx$ 20–30% and above $\approx$ 80–90% density generally not being feasible.

Propagation rates generally decrease with increasing particle size, with ignition often no longer feasible at large (e.g., > 200 μm) particle sizes. Elongated reactant particle shape (e.g., flakes or fibres) parallel to the direction of propagation can also reduce propagation and ignition. In either case, the effects apparently become more substantial as the enthalpy of the reaction decreases. Too small a specimen size or other sources of enhanced local thermal loss can reduce propagation rates while insulation of reactants increase propagation rates. The above effects are, apparently, often less pronounced with more exothermic reactions.

The decreases in propagation rates with increasing density of reactant compacts and increased reactant particle size are attributed to increased local thermal conductivity removing heat from the reaction front. Decreasing access of gaseous reactants may also be a factor in such reactions, e.g., as indicated by higher reaction rates at higher pressures of gaseous reactants. Expansion of unconstrained samples and the presence of liquid phases (and their wetting) may be important. However, much remains to be understood about ignition and propagation.

Data show resultant reacted compositions can be effected by reactant compact microstructure, mainly via the completeness of the reaction. However, limited study has been made, and the possibilities of effecting product character by coating part, or all, of one reactant on particles of one or more other reactants apparently has not been explored at all.

Porosities of constrained reactant compacts where all reactants are solids generally have limited or no effect on the resultant amount of product porosities but large pores are commonly generated in the product compacts due to outgassing during the reaction. Unconstrained specimens often expand; the extent of this generally increasing significantly with the energy released in the reaction as well as increasing with decreasing particle sizes and increasing compact densities. However, detailed studies within a given set of parameters have received little or no attention.

Data to date show particle sizes of reaction compacts generally having limited, or no, effects on reacted product grain sizes. Evidence indicates that residual porosity trapped between grains can limit grain size. However, in compacts not consolidated by pressure during reaction most pores are much larger than the resultant grain size (due to outgassing) and, hence, have limited or no effect on grain size. Evidence to date shows no unusual contiguities of reacted grain structure and a tendency for larger grain sizes relative to conventional processing but more thorough microstructural characterization and study is needed.

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