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13. ABSTRACT (Maximum 200 words)
The beneficial effects of shock-compression of powders and solid-state chemical reactions were utilized to synthesize Ti-Si and Ti-Al intermetallics, Ti-B and Ti-C ceramics, and Ti-Si:Ti-Al composites. Time-resolved stress measurements provided evidence for shock-initiation of reactions in 53% dense Ti-Si powders, based on increased wave speed and volume expansion (due to formation of intermetallic product with higher elastic modulus) measured at shock-pressures exceeding 1.5 GPa. These measurements combined with controlled recovery experiments, revealed the effect of powder morphology and the influence of property differential between reactants on the reaction threshold, demonstrating the dominant role of mechanochemical processes on shock-initiation of chemical reactions. Shock-synthesis was applied to form β -phase C_3N_4 compound using cyano group precursors mixed with azides and iodides. The post-shock reaction behavior of shock-densified Ti-C and Ti-Si powder mixtures was observed to reveal enhanced kinetics with activation energies for diffusion of reactants being lowered by four-to-six times. It was also demonstrated that the shock-activated dense-packed state of powders (elemental reactants or compounds) can be used as an intermediate step for fabrication of net-shaped TiC ceramics, nanocrystalline Ti_5Si_3 intermetallics, and compositionally-graded composites.

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FINAL REPORT

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SHOCK-INDUCED AND SHOCK-ASSISTED REACTION SYNTHESIS OF MATERIALS

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1. STATEMENT OF OBJECTIVES

The combination of high stress, rapid loading rates, and large plastic strains accompanying shock-compression of powders can lead to (a) *shock-induced chemical and structural changes* forming non-equilibrium compounds and metastable phases and (b) *shock-activated dense-packed state of powders* in which the kinetics of post-shock processes is accelerated and the mechanisms are altered. The objective of our research has been to combine the beneficial effects of shock-compression of powders and solid-state chemical reactions to synthesize intermetallic, ceramic, and composite materials with ultra-fine grain microstructures.

To this end, the research conducted during the four year period focussed on several sets of studies, the specific objectives of which are outlined below:

(a) investigation of the mechanisms and kinetics of shock-induced chemical reactions using simultaneous time-resolved stress measurements integrated with controlled recovery experiments in Ti-Si powder mixtures of different particle morphologies;

(b) investigation of the shock-induced reaction behavior of Ti-Si, Ti-Al, and Ti-B powder mixtures to deduce the influence of property differential between reactants;

(c) use of shock-induced chemical reactions for synthesis of non-equilibrium compounds such as theoretically-predicted β -phase C_3N_4 compound;

(d) investigation of transformation (crystallization) behavior of shock-densified Ti-Si amorphous alloy powders for synthesis of nanocrystalline intermetallics;

(e) determination of the enhanced reaction kinetics of shock-densified Ti-C powder mixtures for net-shape fabrication of TiC ceramics; and

(f) Use of shock-assisted reaction synthesis for fabrication of compositionally-graded intermetallic composites.

In the following sections, a summary of key results obtained in the above-mentioned studies will be briefly described. This will be followed by listings of invited presentations, journal and conference proceedings publications, and student thesis awarded. International collaborations were also initiated during the course of the research period. Agreements for collaborative research were signed between Georgia Institute of Technology, and various institutions in Japan. Research work conducted as part of these collaborations will also be described.

2. SUMMARY OF IMPORTANT RESULTS

2.1 SHOCK-INDUCED REACTIONS IN Ti-Si POWDERS: TIME-RESOLVED MEASUREMENTS AND POWDER MORPHOLOGY EFFECTS

The response of porous titanium (Ti) and silicon (Si) powder mixtures with small, medium and coarse particle morphologies was studied under high pressure shock loading, employing post-shock materials analysis as well as nanosecond, time-resolved pressure measurements. The time-resolved measurements of stress pulses obtained with piezoelectric polymer PVDF (poly-vinyl-di-flouride) pressure gauges provided extraordinary sensitivity for determination of rate-dependent shock processes. Both techniques showed clear evidence for shock-induced chemical reactions in medium morphology powders, while fine and coarse powders showed no evidence for reaction. Figure 1 shows a plot of measured input stress versus calculated relative volume and Fig. 2 shows a plot of measured wave speed as a function of measured input stress for medium, coarse, and fine morphology Ti-Si powders. The two plots show deviation of measured points from the calculated inert curve for medium morphology powders, due to rapid shock-induced reaction which increases wave speed and causes expansion of products due to heat of reaction. The fine and coarse morphology powders do not show a similar deviation because of lack of shock-induced reaction in these mixtures within the range of shock conditions explored.

A similar trend of the influence of powder morphology on reaction initiation was also observed from results of controlled shock-recovery experiments, as illustrated in the reaction map shown in Figure 3. It was observed that the medium-morphology powder mixtures experience simultaneous plastic deformation of both Ti and Si particles. Fine morphology powders show particle agglomeration, while coarse Si powders undergo extensive fracture and entrapment within the plastically deformed Ti; such processes decrease the propensity for initiation of shock-induced reactions. The change of deformation mode between fracture and plastic deformation in Si powders of different morphologies, as shown clearly in the SEM micrographs in Figure 4 (a) and (b), was a particularly critical observation. Such a behavior reveals the overriding influence of the shock-induced, visco-plastic deformation and fracture response which controls the mechanochemical nature of shock-induced solid-state chemistry.

The results obtained demonstrate that shock-induced reaction initiation in powders is controlled by solid-state mechanochemical processes, and cannot be qualitatively or quantitatively described by thermochemical models.

2.2 SHOCK-INDUCED REACTION BEHAVIOR OF Ti-Si, Ti-Al, AND Ti-B POWDER MIXTURES - INFLUENCE OF DIFFERENCES IN PROPERTIES OF REACTANTS

The influence of thermochemical properties including heat of reaction and melt temperature in contrast to mechanical property differences between reactants, was studied to elucidate the role of mechanochemical and thermochemical effects on the shock-induced reaction behavior of powder mixtures. Shock recovery experiments were performed on Ti-Si, Ti-Al, and Ti-B powder mixtures to produce compacts of reacted and unreacted states to characterize the reaction product microstructure as well as the shock-compressed configuration of unreacted constituents. Microstructural and x-ray diffraction peak broadening analysis performed on unreacted compacts were used to determine the configurational changes occurring during shock-compression of powders and to quantify the differences in the deformation response of the reactants in each system.

Table 1 lists the properties of reactants for each of the three systems, in which the density differential amongst reactants is essentially similar.

Table 1: Materials Properties of Constituents in the Ti-Al/Si/B System.

PROPERTY	Ti	Al	Si	B
Crystal Structure	hcp	fcc	diamond cubic	rhombohedral
Density (kg/m ³)	4500	2700	2330	2340
Electronegativity	1.5	1.5	1.8	2.0
Melt Temperature(°C)	1670	660	1410	2079
Sound Velocity (m/s)	4970	5300	8500	13900
Yield Strength (MPa)	140	20	93	3
Elastic Modulus (GPa)	70	62	112	440
Heat of Reaction (J/g.at)	TiAl	-36.5 [1654K]		
and [Reaction Temperature]	Ti ₅ Si ₃	-72.5 [2500K]		
	TiB ₂	-108 [3500K]		

Table 2 lists the general experimental results, which can be summarized as follows. The shock-induced reaction behavior of Ti-Si, Ti-Al, and Ti-B powder mixtures is influenced by the deformation response of constituents which is affected by the property differences amongst reactants. Ti-Si powder mixtures show simultaneous deformation of both reactants, and thus provide an optimal configuration of reactants for initiation of shock-induced chemical reactions.

Table 2: Experimental Parameters and Results of Recovery Experiments in Ti-Si, Ti-Al, Ti-B.

	Experiment Number	Packing Density		Configuration	Reaction Behavior
		g/cm ³	(%)		
Ti-Si	NMG-9122	1.92	52.8%	PB-B (5 GPa)	none
	NMG-9120*	1.95	53.6%	MB-B (7.5 GPa)	complete
	2506**	1.912	52%	gun (\approx 5 GPa)	none
Ti-Al	NMG-9305	1.963	51.9%	PB-B (5 GPa)	none
	NMG-9303	2.009	53.1%	MB-B (7.5 GPa)	none
	NMG-9304	1.999	52.8%	MBA-CB (22 GPa)	local rxn.
Ti-B	NMG-9302	2.008	54.0%	PB-B (5 GPa)	none
	NMG-9306	1.962	53.2%	MB-B (7.5 GPa)	none
	NMG-9307	1.953	52.7%	MBA-CB (22 GPa)	complete

*Gun experiment with \approx 380m/s impact velocity using capsule design similar to PB-B configuration.

In Ti-Al powder mixtures having unusually large differential in yield strength, the Al particles are deformed at significantly low pressures forming a fluid-like matrix for subsequent hydrostatic deformation of Ti resulting in limited mixing between the reactants, and thus no reaction. In Ti-B powder mixtures, B particles undergo increasing fracture and fragmentation as a function of shock pressure with the fragments of B becoming engulfed within the deforming Ti, thus providing intimately mixed constituents.

Comparing the reaction propensity of Ti-Si, Ti-Al, and Ti-B powder mixtures under similar shock-loading conditions, it was seen that Ti-Si mixtures have the lowest threshold, followed by Ti-B, and then Ti-Al, irrespective of the differences in the thermodynamic characteristics of these systems. The differences in the mechanical properties of the reactants influence the shock-compression response (deformation or fracture and flow behavior) and mixing of reactants, and therefore the configuration changes prior to initiation of shock-induced reactions. Thus, the results demonstrate that shock-induced reactions are dominated by mechanochemical processes which are influenced by *differences* in the shock-compression response of the powder mixture reactants.

2.3 SHOCK-INDUCED SYNTHESIS OF β -PHASE C_3N_4 COMPOUND

The metastable tetrahedral phase of carbon nitride (β - C_3N_4) has been predicted, both by an empirical scaling relationship and by a pseudo-potential total energy calculation, to have bulk modulus approaching that of diamond and exceeding that of cubic boron nitride. Synthesis of this

theoretically predicted super-hard material is complicated because, unlike diamond, it involves two chemical components: sp^3 -bonded carbon and sp^2 -bonded nitrogen. Several attempts have been made to synthesize carbon nitride using a variety of techniques. Most of these approaches, in general, have resulted either in the formation of hydrogenated or partially crystalline compounds, or at best non-stoichiometric (nitrogen deficient) compounds.

In the present work, shock compression of carbon-nitrogen precursors was used for the synthesis of the theoretically predicted β -phase C_3N_4 compound. Organic precursors containing no H but excess N were identified for shock-synthesis of carbon-nitride compounds. The precursors include combinations of sodium azides [NaN_3] and carbon tetra-iodide [CI_4] mixed with cyano group compounds including sodium dicyanamide [$NaN(CN)_2$] and tetracyanoethylene [$C_2(CN)_4$]. Shock-compression experiments were performed on these precursors blended with ~ 95 wt% Cu powder, statically pressed in steel capsules (at two different packing densities), and impacted under conditions of varying shock amplitude and pulse duration. The shock-compressed samples prepared under different conditions of peak pressure and duration, were acid treated to dissolve metallic copper and other salts, and analyzed via x-ray diffraction, Raman and IR spectroscopy, and TEM/EDS analysis.

Figure 5 shows IR-spectroscopy traces of typical recovered samples shock-compressed with two different pulse durations, showing the presence of amorphous and crystalline C-N compound. The peak positions for β -phase C_3N_4 were inferred from the published IR spectrum of β - Si_3N_4 . Assuming IR lines to be associated primarily with Si-N stretching motions, the shifts in lines were predicted for β - C_3N_4 . The scaling factor was considered to be the ratio of stretching frequencies (μ) related to reduced-mass (ω) ratios for β - Si_3N_4 and β - C_3N_4 $\{ \omega_{Si-N} / \omega_{C-N} = (\mu_{C-N} / \mu_{Si-N})^{1/2} \}$. The yield of β -phase was observed to increase with duration of the shock pulse, which was revealed by an increase in the intensity of the corresponding IR peaks as shown in Figure 5 (b). Plasmon loss energy spectra of EELS performed on nitrogen-containing regions of these samples, indicated sp^3 hybridization, confirming the presence of diamond-like short-range order in the shock-synthesized material.

2.4 SYNTHESIS OF NANOCRYSTALLINE Ti_5Si_3 BY CRYSTALLIZATION OF SHOCK-DENSIFIED Ti-Si AMORPHOUS ALLOY POWDERS

Nanocrystalline microstructures can have profound effects on elastic and plastic mechanical properties, which can give rise to the next generation of materials with high-specific modulus and high strength-to-weight ratio; durable and damage-tolerant systems with combined strength, toughness, wear, and fatigue resistance larger by orders-of-magnitude than that possible with conventional materials; and the ability for superplastic forming to fabricate structural components

with intricate shapes and designs. However, the development of such materials has been hampered due to the inability to fabricate such solid-density materials in bulk form with uniformity of structure, composition, interphase, and grain size, and the lack of fundamental understanding of deformation mechanisms associated with nano-scale microstructures based on aspects of dislocation activity and shear localization. Our objective is to fabricate bulk polycrystalline compacts of multi-phase/multi-component nanocrystalline intermetallics and ceramics for potential applications in armor, aircraft structures, penetrators and cutting tools.

In our preliminary work, dynamic densification was used to consolidate mechanically amorphized Ti-Si alloy powders, using a 3-capsule, plate-impact, gas-gun loading system at velocities of 300, 500, and 700 m/s. The recovered amorphous compacts were subsequently annealed above the crystallization temperature, which was measured by differential thermal analysis (DTA) to be $\sim 600^\circ\text{C}$. In contrast to the uncompacted amorphous alloy powders, the dynamically-densified powder compacts were observed to crystallize to a typically single-phase Ti_5Si_3 compound with ultra-fine grain microstructure, based on TEM and XRD analysis. The average grain size changed from $\sim 40\text{-}50$ nm upon heat treatment at 800°C , to a stable grain size of $90\text{-}100$ nm at temperatures as high as 1400°C (8 hours). In-situ crystallization studies performed by heating the dynamically-densified samples in the TEM at temperatures up to 950°C , revealed that increased crystallization was occurring, not via the growth of the crystallites, but by the increased number density of the nucleating crystallites. Consequently the growth of the crystallites may be inhibited by the impingement of the crystals. Vickers microhardness measurements showed a peak value of ~ 1400 kg/mm² for a grain size of ~ 80 nm, following which a decrease in hardness to ~ 1300 kg/mm² was observed with further increase in grain size. Figure 6 shows plots of microhardness plotted as a function of grain size with (a) direct and (b) Hall-Petch type dependence. The initial increase in hardness with increasing grain size is due to sintering as porosity is decreased with increasing heat treatment temperature. The subsequent decrease following the peak value may be indicative of the Hall-Petch type dependence of hardness on grain size, however, since the grain size did not grow beyond 100 nm, it was not possible to clearly delineate the dependence. While the Vickers microhardness values are $\sim 80\%$ higher than that for microcrystalline shock-densified Ti_5Si_3 alloy, the fracture toughness was measured to be typical of that of brittle ceramics. The low fracture toughness values may be due to dissolved gaseous impurities such as oxygen and nitrogen.

This work is being continued in the new program, in which both Ti-Si and Ni-Ti based nanocrystalline intermetallic compounds are being investigated.

2.5 ENHANCED REACTION KINETICS OF SHOCK-DENSIFIED Ti-C POWDER MIXTURES FOR NET-SHAPE FABRICATION OF TiC CERAMICS

The effect of shock compression on the solid-state chemical reactivity of titanium and carbon powder mixtures was investigated with the objective of forming net-shaped TiC ceramics with a fine-grain microstructure. Elemental titanium and carbon (graphite) powder mixtures were shock-compressed, as well as statically densified, to make ~90% dense green compacts for subsequent reaction synthesis. The synthesis experiments were performed in an induction-heated hot press at temperatures of 0.6-0.8 of T_m of titanium, with hold times of 30 to 180 minutes, and a nominal pressure of 34.5 MPa (5000 psi).

The combination of defect states and intimate interparticle contacts, introduced during shock-compression, results in significant enhancement in the solid-state chemical reactivity of Ti and C. Consequently, the post-shock reaction behavior of the shock-densified Ti-C powder mixture compacts is dominated by defect-enhanced solid-state diffusion. The reaction product formation rates were determined using metallographic measurement of reaction layer thickness (converted to volume fraction) as well as XRD determination of overall volume fraction as a function of time and temperature. Measurements of reaction layer thickness showed the progress of reaction following the Avrami growth kinetics. A reaction kinetics model based on the theoretical consideration developed by Jander and subsequently modified by Carter, in which a solid particle of a given radius undergoes reaction with another component at the surface via a diffusion controlled process, was used to determine the kinetics of the overall synthesis process. The model also considered the change in volume accompanying the conversion of reactants to products. The results revealed that the otherwise-sluggish diffusion of Ti and C through the TiC_x boundary layer was significantly enhanced in the shock-compressed powder mixtures.

Measurements of the volume fraction of reacted material fitted to Carter's reaction kinetics model are shown in Figure 7. The reaction rate constant obtained from these results was applied to varying range of particle sizes (6-11 μm), yielding an activation energy of ~32.4 kJ/mole, which is two-to-three times lower than diffusion of carbon into TiC_x and about four times lower than diffusion of Ti into TiC_x . As a result, triangular-shaped sections (with sharp edges and rounded corners) of shock-densified compacts (>85% dense) were reaction synthesized in the solid-state, producing microstructures with equiaxed grains of <6 μm size and microhardness of ~2000 kg/mm². In contrast, statically pressed Ti + C powder compacts of same initial density showed reaction synthesis dominated by a combustion-type process (following initial solid-state diffusion). The resulting reaction synthesized statically-pressed compacts showed a highly porous reaction product, typical of that produced during self-propagating high-temperature synthesis. Shock-compression of powders, thus, not only assists in providing a high-green-strength reactant compact, but also activates the constituents to ensure reaction synthesis in the solid-state.

2.6 SHOCK-ASSISTED REACTION SYNTHESIS OF Ti-Si and Ti-Al FUNCTIONALLY-GRADED INTERMETALLIC COMPOSITES

The reaction behavior of shock-densified intermetallic-forming Ti-Si powder mixture compacts was studied to investigate fabrication of functionally-graded intermetallic-ceramic composites with fine-grained microstructures. Compacts of similar density were also made by uniaxial pressing at 50,000 psi (~0.78 GPa) to compare their reaction behavior with those made by shock compression. The shock-densified Ti-Si powder mixture compacts react via defect-enhanced solid-state diffusion producing a Ti_5Si_3 compound with a grain size $\sim 3 \mu m$, and a hardness of ~ 791 VHN. Based on a transient heat flow model, it was determined that the heat released due to the solid-state reaction in the shock-densified compacts is rapidly dissipated in the dense compacts which minimizes local temperature increase. In statically-pressed powders, the retention of heat results in increase in local temperature and causes the reaction to be taken over via a combustion process which yields a product having significant retained porosity.

Figures 8 (a,b) show SEM micrographs of fracture surfaces comparing the reaction behavior of uniaxially pressed Ti-Si samples and shock-densified compacts after heat treatment in the furnace at $1300^\circ C$ for 3 hours. It can be seen that the uniaxially-pressed samples show a large amount of porosity formed primarily due to the initially porosity and that associated with volume change between reactants and products. The shock-densified samples have higher initial density, and the porosity due to volume change is accommodated by their solid state diffusion to surfaces, thereby yielding final reacted compacts of $>96\%$ density.

Based on the understanding gained from the reaction behavior of shock-densified Ti-Si powder mixtures, a shock recovery experiment was performed using the newly designed single-capsule gas gun fixture to demonstrate the viability of making a functionally gradient material (FGM) compact. The sample consisted of four pre-packed layers of Ti-Si and Ti-Al powder mixtures with varying amounts of each constituent in different layers; the impact face being pure Ti-Si (~ 2 mm thick, and $\sim 48\%$ dense) while the opposite face was a 40-60 vol% mixture of Ti-Si and Ti-Al (~ 1.4 mm thick and $\sim 61\%$ dense). The two intermediate layers were 80-20 (~ 1.6 mm thick, $\sim 53\%$ dense) and 60-40 vol% (~ 1.3 mm thick, $\sim 61\%$ dense) Ti-Si and Ti-Al powder mixtures, respectively. The sample cavity in the single capsule shock-recovery fixture had a diameter of ~ 2.5 inches and a depth of 0.362 inches. A 0.115 inch cover plate was used in combination with a 10 mm thick flyer plate. The impact velocity was measured at 520 m/s. The density of the shock-compressed sample was found to be 3.619 g/cc which is 99.8% of the average density of the FGM sample. Microstructural characterization of the sample revealed a predominantly void-free shock-densified compact. The shocked-densified samples were then subjected to different heat treatments to study the reaction characteristics of the reaction synthesized FGM. Several treatments were performed with a final temperature greater than the melting point of Al, to first initiate a Ti-Al reaction which

would consequently result in reaction between Ti and Si. Treatments with a final temperature less than the melting point of Al were also conducted, in which case only partial reaction was observed. X-ray diffraction analysis of the sample subjected to 600°C with 60 minute hold time followed by heating to 700°C for 5 minutes gave the best results in terms of complete reaction with minimal porosity. The SEM micrographs shown in Figure 8, reveal the general microstructure of the four layers. It can be seen that all the four layers are fully dense, albeit with different morphologies, grain sizes, and microhardness values: 100 % Ti-Si layer (10-15 μm and $\text{VHN}=803 \text{ kg/mm}^2$), 80-20 % Ti-Si:Ti-Al layer (5-10 μm and $\text{VHN}=628 \text{ kg/mm}^2$), 60-40 % Ti-Si:Ti-Al layer (5-10 μm and $\text{VHN}=573 \text{ kg/mm}^2$), and 40-60% Ti-Si:Ti-Al layer (less than 5 μm and $\text{VHN}=504 \text{ kg/mm}^2$). These results provide the basis of the work to be performed in the new program, in which shock-assisted reaction synthesis will be used to form the intermetallic matrix, and ceramics such as Si_3N_4 and c-BN will be used as the superhard reinforcements.

3. CONCLUSIONS

The following conclusions are drawn from the results of the studies performed in this research:

(I) Combined time-resolved stress measurements and microstructural analysis of samples obtained from shock recovery experiments provide an important tool for obtaining evidence of shock-induced chemical reactions. The measured increases in wave speed through Ti-Si powders at pressures above 1.5 GPa, provide clear evidence of shock-initiation of reactions. The influence of powder particle size and initial porosity on the propensity of reaction initiation, confirmed the mechanochemical nature of shock-induced reactions. Shock-synthesis of β -phase C_3N_4 was demonstrated starting with cyano group precursors mixed with azides and iodides, based on results of infra-red spectroscopy and plasmon loss energy spectra of EELS indicating sp^3 hybridization.

(ii) Bulk compacts of Ti_5Si_3 intermetallic with $<95 \text{ nm}$ grain size were obtained by crystallization of shock-densified Ti-Si amorphous alloy powders. The shock-induced defects allow autocatalytic nucleation of crystallites, permitting retention of nano-structure. Compacts have microhardness values of 1400 kg/mm^2 , which are twice as that of conventional materials, however, they have low fracture toughness ($2\text{-}3 \text{ MPa}\cdot\text{m}^{1/2}$), possibly due to presence of impurities.

(iii) Shock-densified Ti+C powder compacts undergo reaction synthesis via defect-enhanced solid-state diffusion with activation energies for diffusion of constituents lowered by four-to-six times. A Ti_5Si_3 -TiAl compact with functionally-graded composition was prepared also prepared using the shock-assisted reaction synthesis approach, demonstrating the potential of making FGM composites.

4. LIST OF INVITED PRESENTATIONS

1. N.N. Thadhani, "Solid-State Shock Chemistry: Mechanistic Aspects," Energetic Materials Research Committee Meeting of the United Kingdom, Srivenham, England, Sept 30, 1993.
2. "Solid-State Aspects of Shock Chemistry," National Institute of Materials and Chemicals Research, Tsukuba, Japan, December 18, 1993.
3. "Process Mechanisms of Shock Synthesis of Materials," Physics Colloquium, Washington State University, March 1, 1994.
4. "X-ray Diffraction Line-broadening Analysis of Shock-Compressed Powder Mixtures," Sandia National Laboratories, Albuquerque, October 18, 1994.
5. "Shock-activated Synthesis of Intermetallics and Ceramics," Symposium on Processing and Fabrication of Advanced Materials, TMS/ASM Fall Meeting, Cleveland, October 1995.
6. "Shock-Induced and Shock-Assisted Synthesis of Intermetallics and Ceramics," Symposium on Advances in Shock-Compression Science, Sandia National Laboratories, Albuquerque, June 4, 1996.
7. "Mechanistic Processes Influencing Solid-state Shock Chemistry and Shock Synthesis of Materials, Symp. on Shock-Induced Chemical Processing, St. Petersburg, Russia, June 1996.
8. "Dynamic High-pressure Synthesis and Processing of Wear-resistant and Refractory Materials" Workshop on "Hot Gas Erosion and Wear of Materials, University of Michigan, September 25-27, 1996.
9. "Materials Synthesis by Shock-Induced and Shock-Assisted Reaction Processes," International Conference on Condensed Matter under High Pressures, Bhabha Atomic Research Center, Bombay, India, Nov 11-15, 1996.
10. "Shock-induced and Shock-assisted Synthesis of Hard Materials," Physics Colloquium, University of Alabama, Birmingham, January 31, 1997, **invited**.
11. "Shock-induced and Shock-assisted Reaction Synthesis of Intermetallics and Ceramics," TMS Symposium on P/M Current Research and Industrial Practices, Fall Meeting, Indianapolis, Sept 14-18, 1997.
12. "Shock Assisted Synthesis of Ti_3Si_3 Intermetallic Alloy," International Workshop on Industrial Applications of Explosions, Shock-Waves, and High-Pressure Phenomena, Kumamoto University, Kumamoto, Japan, October 27-28, 1997.

5. LIST OF RESEARCH PUBLICATIONS

1. E. Dunbar, R.A. Graham, G.T. Holman, M.U. Anderson, and N.N. Thadhani, "Time-Resolved Pressure Measurements in Chemically Reacting Powder Mixtures," in High-Pressure Science and Technology -1993, ed. S.C. Schmidt, J.W. Shaner, G.A. Samara, and M. Ross, American Inst. of Phys. Conf. Proc. 309, Part II, 1994, pp.1303-1306.
2. N.N. Thadhani, E. Dunbar, and R.A. Graham, "Characteristics of Shock-Compressed Configuration of Ti-Si Powder Mixtures," in High-Pressure Science and Technology - 1993, ed. S.C. Schmidt, J.W. Shaner, G.A. Samara, and M. Ross, American Inst. of Physics Conference Proc. 309, Part II, 1994, pp. 1307-1310.
3. N.N. Thadhani, "Shock-Induced and Shock-Assisted Solid-State Chemical Reactions in Powder Mixtures, J. Appl. Phys., 76 (4) (1994) 2129-2138.
4. T.E. Royal and N.N. Thadhani, "Shock-Induced Reaction Behavior of Ti-Si and Ti-B powder Mixtures," in Metallurgical and Materials Applications of Shock Wave and High-Strain-Rate Phenomena, eds., L.E. Murr et al. Elsevier Science, 1995, pp. 629-636

5. T. Royal, S. Namjoshi, and N.N. Thadhani, "Mechanistic Processes Influencing Shock Chemistry in Ti-Al/Si/B System," Metallurgical and Materials Transactions, Vol. 27A, pp. 1761-1771, 1996.
6. N.N. Thadhani, and R.A. Graham, T. Royal, E. Dunbar, M.U. Anderson, G.T. Holman,, "Shock-Induced Chemical Reactions in Ti-Si Powder Mixtures of Different Morphologies: Time-resolved Pressure Measurements and Materials Analysis," Journal of Applied Physics, 82 (3), (1997), pp. 1113-1128
7. N.N. Thadhani and T. Aizawa, "Materials Issues in Shock Compression Induced Chemical Reactions in Porous Solids," in Shock-Compression of Porous Solids, (L.E. Davison, M. Shahinpoor, and Y. Horie, eds.), Springer-Verlag, (in press).
8. N.N. Thadhani, "Materials Synthesis by Shock-Induced and Shock-Assisted Reaction Processes," in Proceedings of International Conference on Condensed Matter under High Pressures, Bhabha Atomic Research Center, Bombay, India, Nov 11-15, 1996, in press.
9. J.-H Lee and N.N. Thadhani, "Reaction Synthesis Mechanism in Dynamically Densified Ti+C Powder Compacts," Scripta Materialia, in press.
10. S.A. Namjoshi and N.N. Thadhani, "Reaction Synthesis of Shock-Densified Ti-Si Powder Mixtures," in Shock-Compression of Condensed Matter -1997, eds. S.C. Schmidt et al., AIP press, in press, 1997.
11. P.J. Counihan, A. Crawford, and N.N. Thadhani, "Nanostructure Formation by Dynamic Densification and Recrystallization of Amorphous Ti-Si Alloy," in Shock-Compression of Condensed Matter -1997, eds. S.C. Schmidt et al., AIP press, in press, 1997.
12. P. Counihan, A. Crawford, and N.N. Thadhani, "Shock Assisted Synthesis of Ti_5Si_3 Intermetallic Alloy," Proc. Of International Workshop on Industrial Applications of Explosions, Shock-Waves, and High-Pressure Phenomena, Kumamoto University, Kumamoto, Japan, October 27-28, 1997, in press.
13. J.-H. Lee and N.N. Thadhani, "Enhanced Solid-State Reaction Kinetics of Shock-Compressed Ti and C Powder Mixtures," to be submitted to Journal of Mater. Res., Nov'97.
14. P. Counihan, A. Crawford, and N.N. Thadhani, "Influence of Dynamic Densification on Nanostructure Formation in Ti_5Si_3 Intermetallic Alloy and its Properties," to be submitted to Metallurgical and Materials Transactions, December 1997.

6. LIST OF PERSONNEL INVOLVED AND DEGREES AWARDED

1. Prof. Naresh Thadhani, Principal Investigator
2. Prof. Kazuyuki Hokamoto, Kumamoto University, "Characterization of Interfaces in Explosively Cladded Ti-Al Layers" January to May, 1996,
3. Tyrus Royal, "Investigation of Mechanisms of Shock-Induced Chemical Reactions in Ti-Al, Ti-B, and Ti-Si Powder Mixtures," Completed M.S. in December 1994.
4. Jong-Heon Lee, "Synthesis of TiC by Shock-Assisted Solid-state Reaction Sintering," Ph.D. Dissertation, completed in December 1996.
5. Patrick Counihan, "Nanocrystalline Ti-Si alloy formation by shock-densification and crystallization of mechanically amorphized compounds", completed M.S. in June 1997.
6. Shantanu Namjoshi, "Shock Assisted Reaction Synthesis of Ti-Al-Si and Ti-Al-B Intermetallic-ceramic Composites," Ph.D. in progress (expected Summer '98).
7. Rodney Russell, "Time-Resolved Diagnostics for real-time measurements," Undergraduate Independent Research, in progress.
8. Alice Crawford, "Crystallization Behavior of Shock-Densified Ti-Si Powder Mixtures," undergraduate independent Research, in progress.

7. FACILITIES DEVELOPED

The Georgia Tech gas gun is a state-of-the-art high-strain-rate facility equipped with interferometric, stress-gauge measurement, and high-speed digital data acquisition instrumentation, built with funding received from Georgia Tech through faculty start-up funds (of Naresh Thadhani, MSE, and Min Zhou, ME), and from the Army Research Office through the DURIP program. This facility allows material testing to be conducted for strain rates up to 10^6 s^{-1} , under a range of multiaxial states of stress through normal and pressure-shear (inclined) plate impact experiments. The single-stage gas gun has an 80 mm diameter, 8 m long gun barrel connected to a 28.5 liter gas chamber separated via a double (rupture) diaphragm on the breech side and connected to a large soft-recovery catcher tank on the muzzle side. Impact velocities between 100 to 1200 ms^{-1} (reproducible within 5%) can be obtained, and are monitored using four sets of arrival-time velocity pins, connected to a Tektronix Model 640 digitizing oscilloscope and digital counters (HP Model No. 5313A, 2 channel, 225 MHz). The large gun barrel diameter allows observations to be made under pure plane strain conditions for up to 15 ms. This clean and well-characterized condition is very important in the interpretation of experimental data and the formulation of constitutive relations. The sample test fixture is held directly on to the lapped surface of a sacrificial plate allowing controlled experiments to be performed with impact planarities better than 50 milli-radians. The well-designed specimen recovery mechanism, allows time-resolved *in-situ* pressure measurements to be performed using PVDF stress gauges, and particle velocity measurements using VISAR interferometry. The state-of-the-art VISAR (Velocity Interferometer System for Any Reflector) equipment, recently been acquired for free surface velocity measurement, has a sensitivity of 2 ms^{-1} and a depth of field of 12 mm. Velocities in the range of 30-5000 ms^{-1} can be measured. Two four-channel Tektronix digital oscilloscopes (Model TDS784A) with a sampling rate of 4 Giga points per second are available for high speed data acquisition.

Its should be noted that this gas gun facility has developed as a major high-strain-rate capability at Georgia Tech. It is now a part of the Institute wide Mechanical Properties Research Laboratory, and is used by faculty from the School of Materials Science and Engineering as well as Mechanical Engineering. On an annual basis research projects totaling more than \$500,000 are utilizing this capability. The research projects are funded by the Army Research Office, the Air Force Office of Science and Technology, and the Office of Naval Research, in addition to contracts from several small companies.

8. INTERNATIONAL COLLABORATIONS

During the last four years extensive international collaborations were initiated with institutions in Japan. Agreements for research collaboration and scientific exchange were signed between Georgia Tech and The University of Tokyo, Kumamoto University, and the National Institute of Materials and Chemicals Research in Tsukuba. As a result of this, there was exchange of scientists at different levels and the principal investigators made frequent visits to respective institutions to discuss about the latest developments in their research activities. Joint experiments were also performed, making use of unique facilities of each institution. These have now become an ongoing activity and is expected to continue in the future.

The collaboration with the University of Tokyo has involved interactions with Prof. Tatsuhiko Aizawa, who has developed unique facilities for rapid mechanical milling of powders, which is observed to show low threshold for shock-induced reaction synthesis. Our collaboration has included exchange of information before results are published, defining of approaches to pursue common goals, conducting of shock-compression experiments performed using the Georgia Tech gas gun on powder mixtures prepared with the rapid milling set-up at the University of Tokyo, and joint publication of papers.

Collaboration with the Kumamoto University has involved exchange of scientists in addition to performing joint experiments. Professor Kazuyuki Hokamoto spent five months (January 1996 to May 1996) as a visiting scientist at Georgia Tech. He worked on characterization of interfaces in explosively clad Ti-Al layers for the purpose of investigating shock-induced reactions in solid-density materials. Following this, Dr. Jong-Heon Lee, who graduated with a Ph.D. from Georgia Tech accepted a post-doctoral scientist position at Kumamoto University, starting on March 1, 1997. Prof. Hokamoto and Dr. Lee are currently working on shock-induced reactions in Ti-Si powder mixtures using long-duration pressure pulses generated via underwater explosive experiments, which is a capability unique to Kumamoto University.

Collaboration with the National Institute of Materials and Chemical Research has involved interactions with Dr. Masatake Yoshida on time-resolved temperature measurements. Dr. Vidya Subramanian, a former post-doctoral research associate in our group at Georgia Tech, spent a five week period (January to February 1995) working with Dr. Yoshida on real-time temperature measurements in Ti-Si powder mixtures. The results of this work were reported in the interim progress report to ARO. In general while quite a lot of data was obtained, reliable interpretation was not possible due to lack of some critical calibration data. It is anticipated that this work will continue in the future. Dr. Yoshida is now working on development of a plasma laser facility for generation of ultra-high pressure (terra pascal range), for studies on materials synthesis and equation of state.

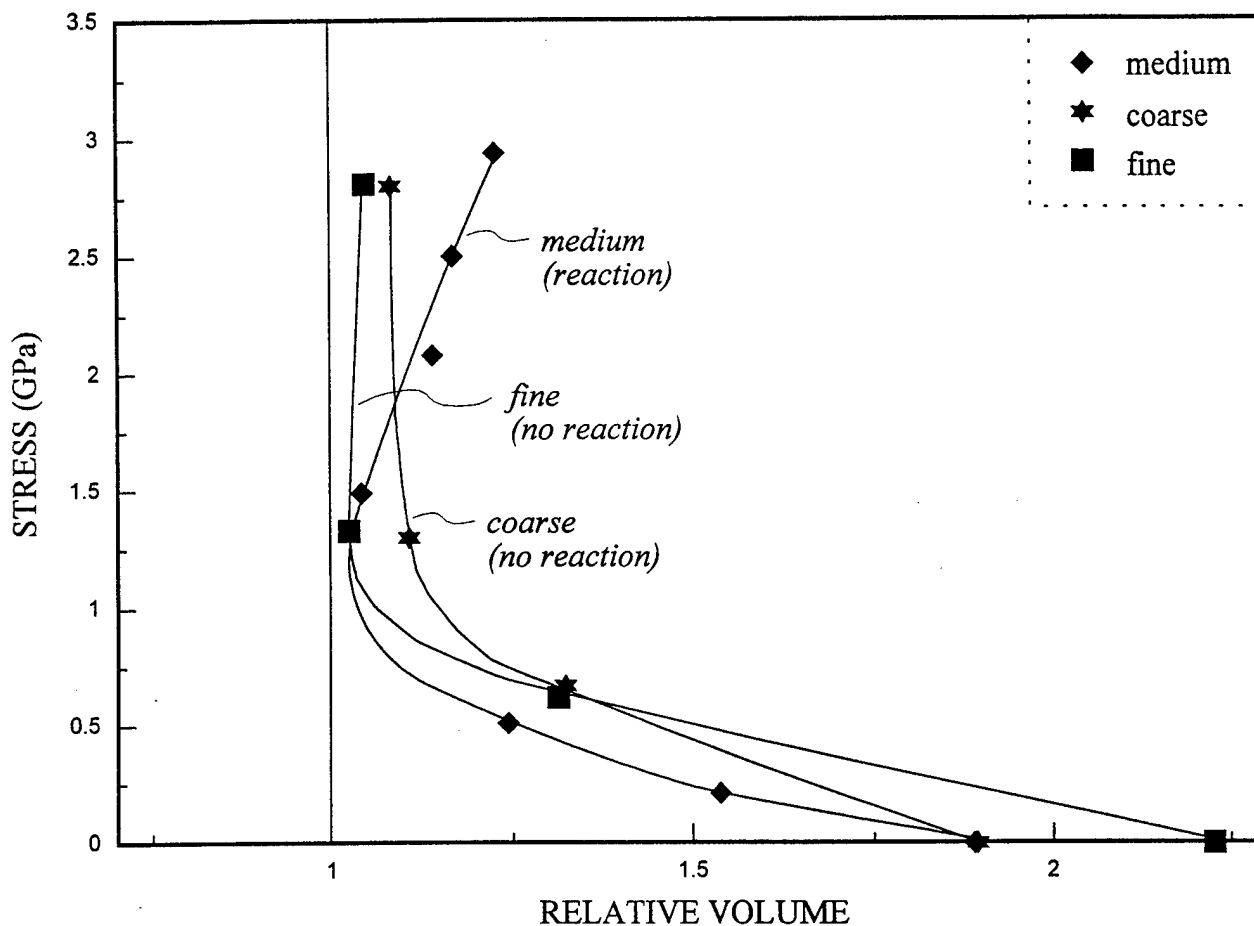


Fig. 1. Measured input stress plotted as a function of calculated relative volume for medium, coarse, and fine Ti-Si powder mixtures, along with a calculated (vertical) curve for a solid inert Ti-Si powder mixture. Points corresponding to experimentally measured input stress and calculated relative volume for the three different morphologies of powder mixtures show significantly different trends. Points for medium morphology powders indicate crush-up to full density at ~ 1 GPa pressure, followed by volume expansion (shift to right of calculated solid inert mixture curve), indicating evidence for rapid shock-induced chemical reaction, while points corresponding to coarse and fine powders show crush up at higher pressures and no significant deviation from solid curve, indicating no reaction at pressures up to 3 GPa.

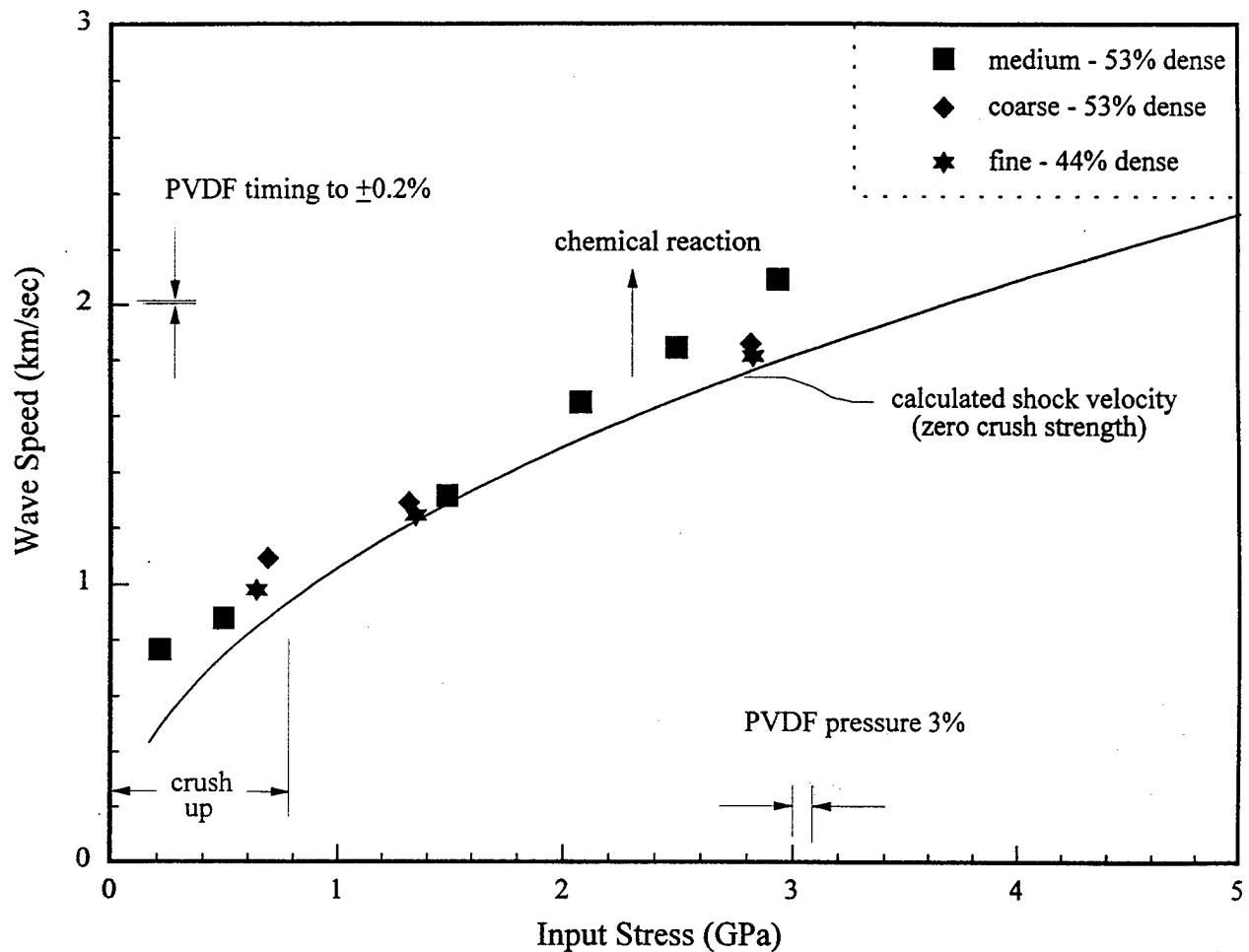


Fig. 2. Plot of experimentally measured wave speed as a function of measured input stress for the three morphologies of Ti-Si powder mixtures showing trends similar to those revealed by pressure-volume compressibility characteristics shown in Figure 1. The points for medium morphology powders approach the calculated curve for the inert powder at the crush-up strength, and at input stresses greater than the crush strength the experimental points deviate from curve showing increased wave speed corresponding to occurrence of chemical reaction and formation of intermetallic compound in the shock state. Points for the fine and coarse mixtures remain close to the calculated curve indicating no reaction.

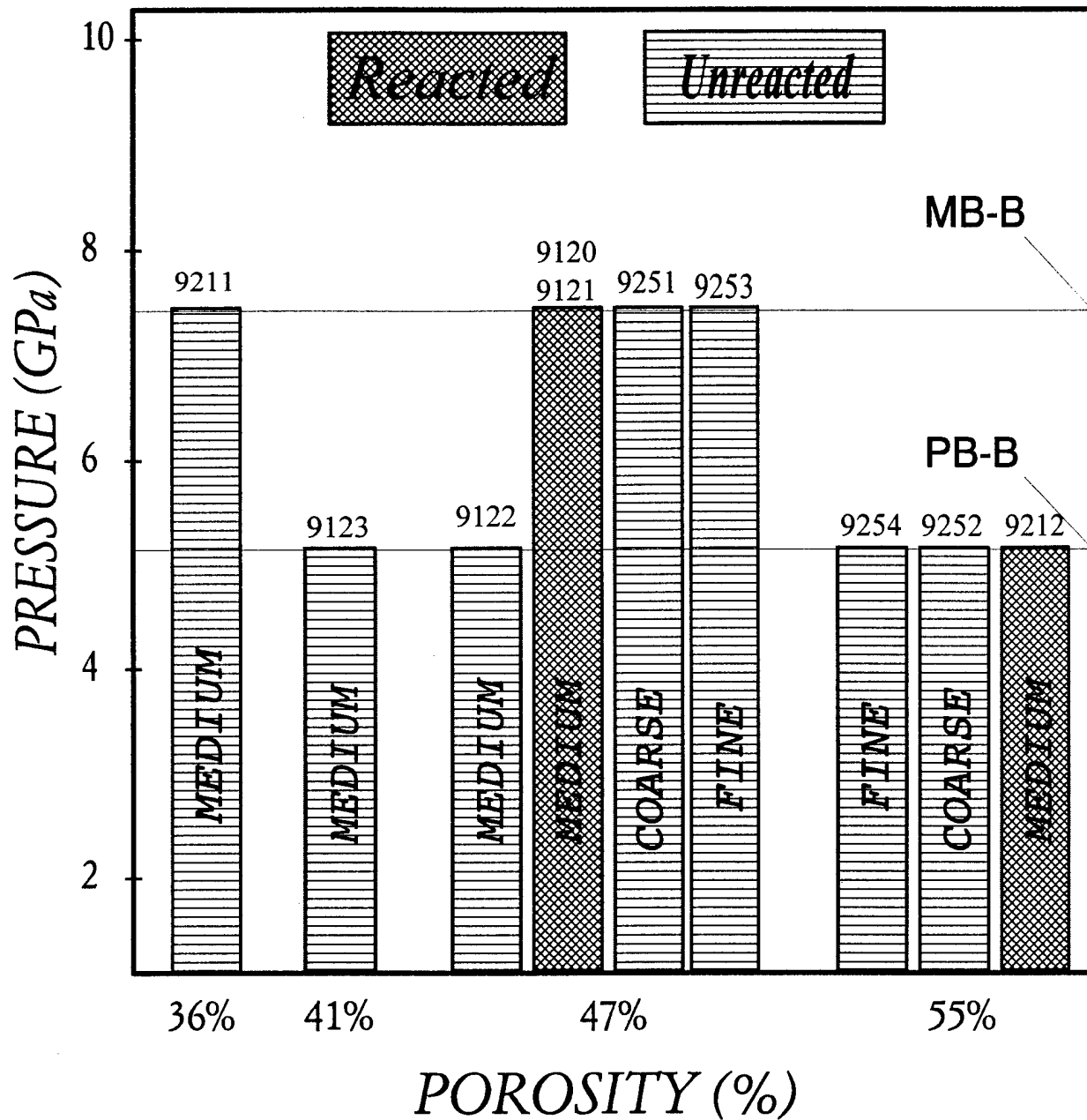


Fig. 3. Reaction map showing overall results of shock recovery experiments, based on effect of initial density and shock pressure on reaction threshold in Ti-Si powder mixtures of medium (Ti, Si = 10-44 μ m), coarse (Ti = 105-149 μ m and Si = 45-149 μ m) and fine (Ti = 1-3 μ m, Si < 10 μ m). Cross-hatched bars correspond to reacted material and horizontally-hatched bars with bold lettering correspond to unreacted material, as evidenced from microstructural (optical and XRD) analysis of recovered shock compressed samples.

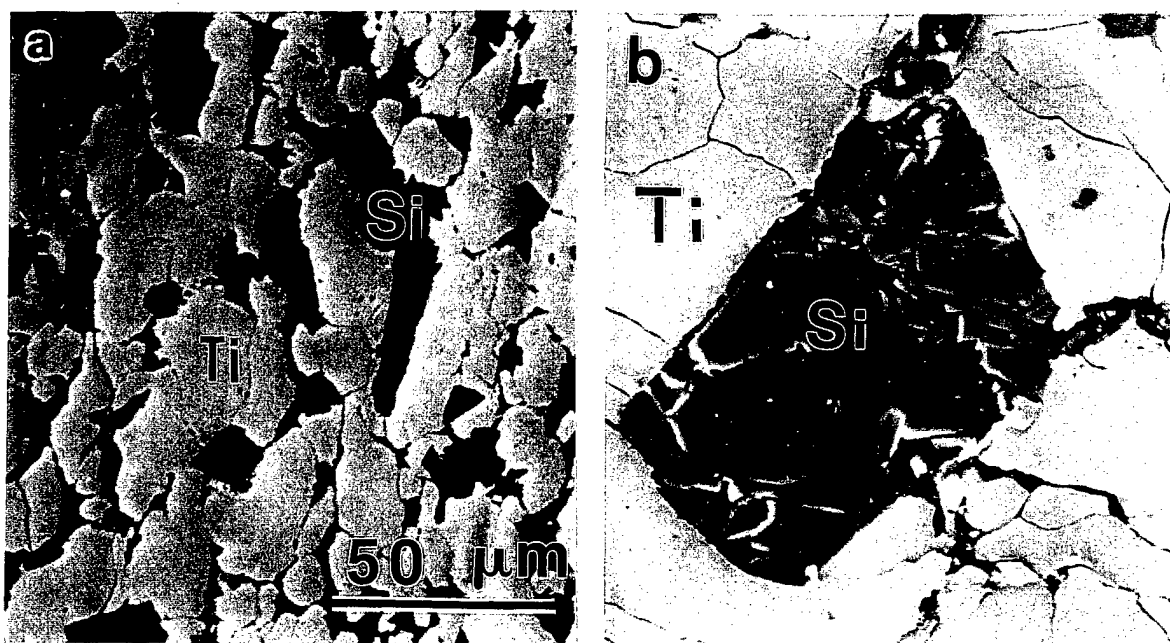


Fig. 4. SEM micrographs showing unreacted configuration of (a) medium morphology and (b) coarse morphology Ti-Si powder mixtures shock-compressed with MBB fixture, revealing the deformation of Ti in both medium and coarse morphology powders, and deformation of medium morphology Si and fracture of coarse morphology Si powders.

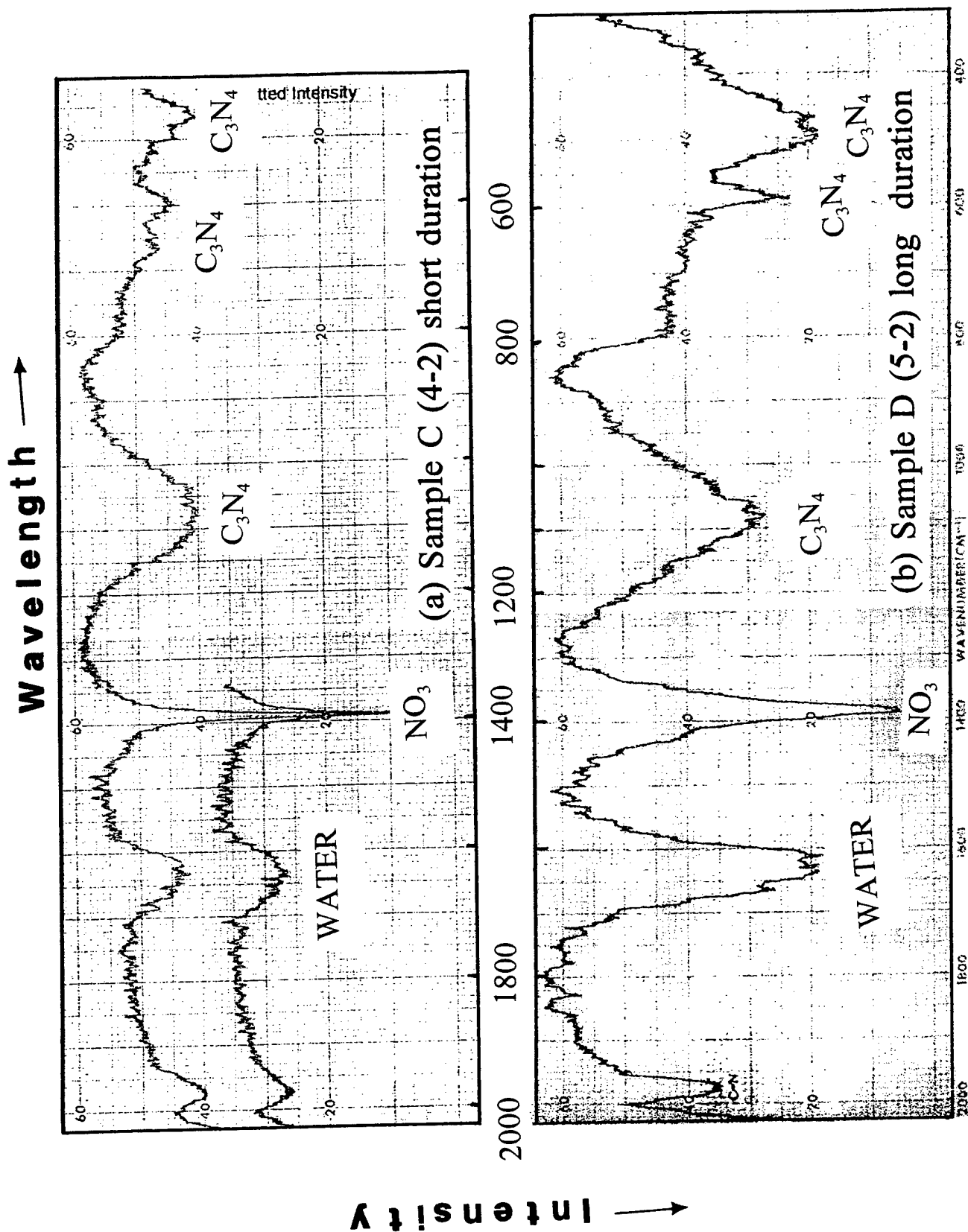


Fig. 5. Infra-red spectra of precursors containing sodium azide [NaN₃] and carbon tetra-iodide [CI₄] mixed with sodium dicyanamide [NaN(CN)₂] shock-compressed at ~40 GPa with 1.8 (short) and 3.6 μs (long) pulse durations.

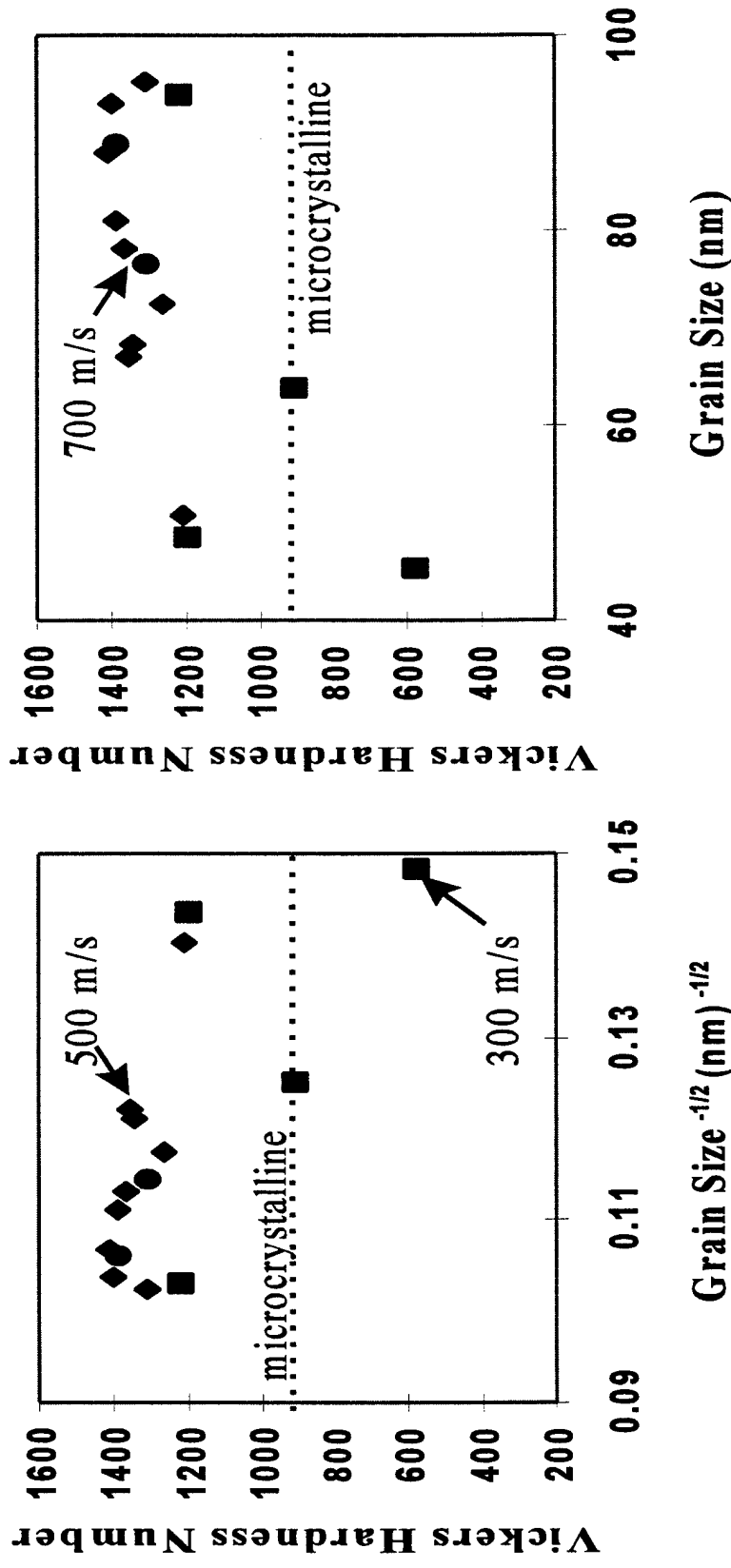


Fig. 6. Variation of microhardness versus crystallite size based on plots showing (a) inverse-square-root Hall-Petch type dependence and (b) direct linear dependence.

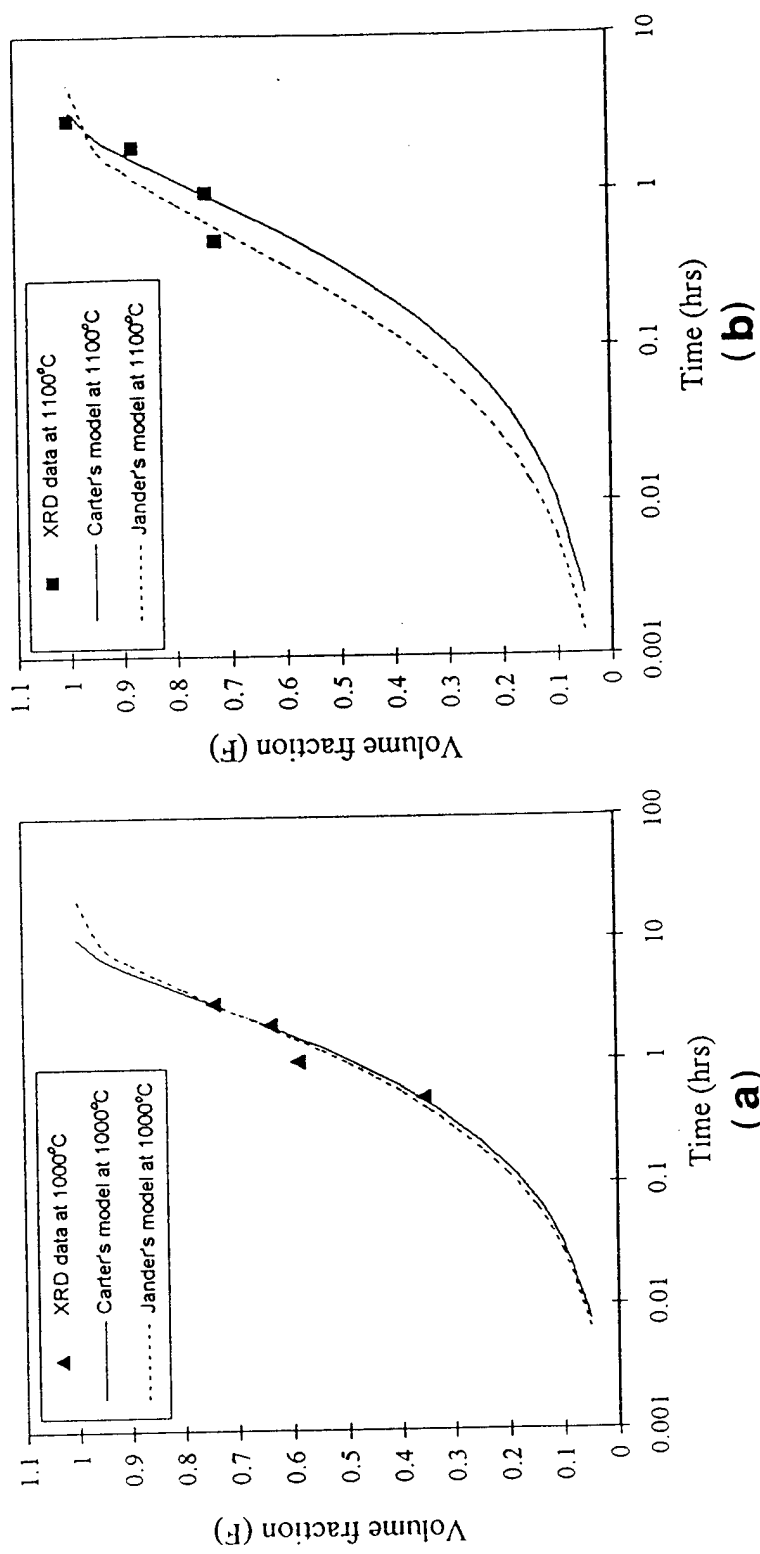


Fig. 7. Plot of measured volume fraction of reacted material as function of time at 1100° and 1200°C showing better fit with Carter's reaction kinetics model. Reaction rate constant applied to range of particle sizes (6-11 μm), yielded activation energy of ~32.4 kJ/mole, which is two-to-three times lower than diffusion of C into TiC_x and about four times lower than diffusion of Ti into TiC_x.

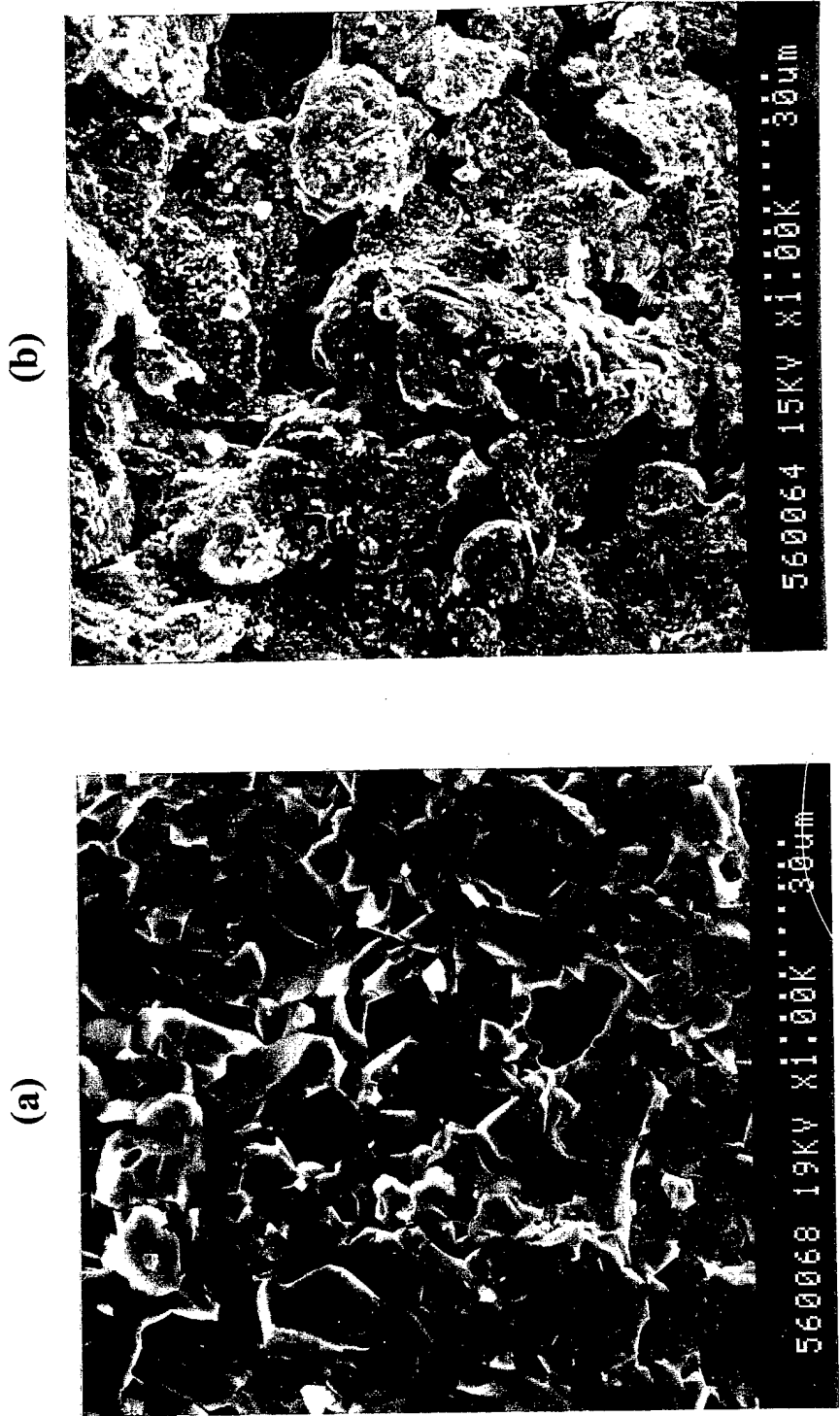
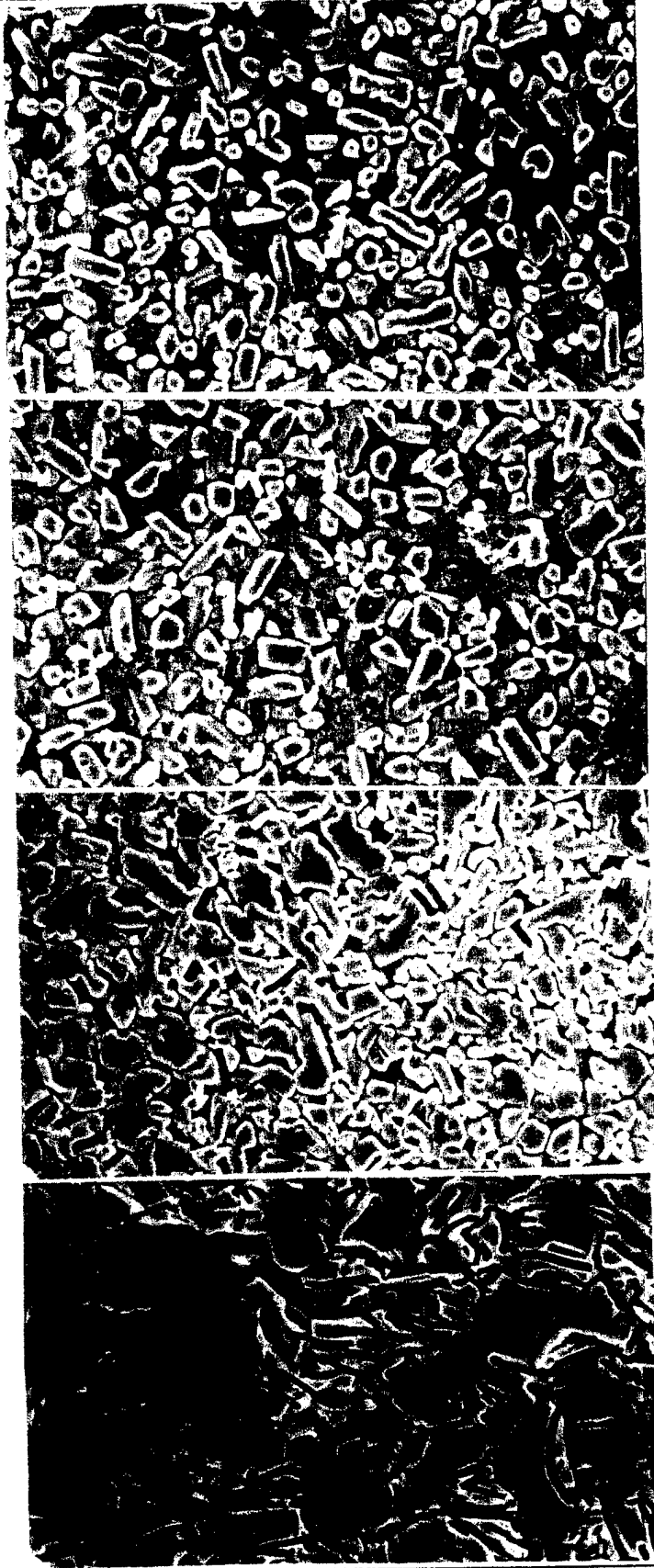


Fig. 8. SEM micrographs comparing reaction synthesized microstructure of (a) uniaxially-pressed sample showing highly porous reaction product and (b) shock-densified Ti-Si compact showing >96% dense product with ~3 μm and a hardness of ~791 VHN.

Impact \rightarrow

30 μm



Ti:Si::Ti:Al - 100:0
VHN = 803 kg/mm²

Ti:Si::Ti:Al - 80:20
VHN = 628 kg/mm²

Ti:Si::Ti:Al - 60:40
VHN = 573 kg/mm²

Ti:Si::Ti:Al - 40:60
VHN = 504 kg/mm²

Fig. 9. SEM micrographs showing high-magnification view of local areas in the shock-compressed Ti-Si::Ti-Al FGM compact, revealing dense (pore-free) and uniform-grained structure following reaction synthesis under Ar atmosphere. (Heat treatment under Ar atmosphere - 20°C/min to 600°C, 1 hour hold, 10°C/min to 700°C, 5 minute hold, followed by 20°C/min cooling rate.)