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11:45:46           OCA PAD AMENDMENT - PROJECT HEADER INFORMATION           06/08/95

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Project #: E-18-692           Cost share #:                        Rev #: 4
Center # : 10/24-6-R8004-0A0  Center shr #:                        OCA file #:
                                                                   Work type : RES
Contract#: N00014-94-1-0169             Mod #: P00002              Document  : GRANT
Prime   #:                                                         Contract entity: GTRC

Subprojects ? : N                                                  CFDA: 12.300
Main project #:                                                    PE #:


Project unit:              MSE          Unit code: 02.010.112
Project director(s):
   THADHANI N N            MSE          (404)894-2651
   PARK B                  MSE          (404)-


Sponsor/division names: NAVY                        / OFC OF NAVAL RESEARCH
Sponsor/division codes: 103                         / 025


Award period:     931201    to    960531  (performance)    960531  (reports)

Sponsor amount          New this change              Total to date
     Contract value         84,900.00                   209,835.00
     Funded                 47,000.00                   171,835.00
Cost sharing amount                                           0.00

Does subcontracting plan apply ?: N

Title: MECHANISMS OF SHOCK-INITIATED INTERMETALLIC REACTIONS


                           PROJECT ADMINISTRATION DATA

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Security class (U,C,S,TS) : U           ONR resident rep. is ACO (Y/N): Y
Defense priority rating   :             ONR supplemental sheet
Equipment title vests with:    Sponsor       GIT X

Administrative comments -
 MOD # P00002 ADDS $84,900 AND EXTENDS GRANT TO 5/31/96 FOR PROPOSAL ENTITLED
 "CONTROLLED SHOCK-INITIATION OF INTERMETALLIC REACTIONS".
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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

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NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 05/31/96

Project No. E-18-692

Center No. 10/24-6-R8004-0A0

Project Director THADHANI N N

School/Lab MSE

Sponsor NAVY/OFC OF NAVAL RESEARCH

Contract/Grant No. N00014-94-1-0169

Contract Entity GTRC

Prime Contract No.

Title MECHANISMS OF SHOCK-INITIATED INTERMETALLIC REACTIONS

Effective Completion Date 960531 (Performance) 960531 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

Comments

Subproject Under Main Project No.

Continues Project No.

Distribution Required:	
Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

NOTE: Final Patent Questionnaire sent to PDPI.

E-18-692
#1

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May 24, 1996

Dr. Richard Miller and Dr. Judah Goldwasser
Mechanics and Energy Conversion, S&T Division
Office of Naval Research,
Ballston Tower One, 800 North Quincy Street
Arlington, VA 22217-5660

Dear Dr. Miller and Dr. Goldwasser:

Enclosed please find a copy of our final report for research performed under the Office of Naval Research Grant entitled MECHANISMS OF SHOCK-INITIATED INTERMETALIC REACTIONS (Contract No. N00014-94-1-0169).

I thank you and the Office of Naval Research for the support of my research activities. Please do not hesitate to contact me, should you need any additional inofrmation on this work.

Yours sincerely,

Naresh Thadhani
Associate Professor
Tel: (404) 894-2651

Copy: David Moore, MSE

MECHANISMS OF SHOCK-INITIATED INTERMETALLIC REACTIONS

Contract # N00014-94-1-0169

FINAL REPORT

Submitted to

Dr. Richard Miller and Dr. Judah Goldwasser
Mechanics and Energy Conversion, S& T Division
Office of Naval Research
Ballston Tower One, 800 North Quincy Street
Arlington, Virginia 22217

by

Naresh N. Thadhani, Vidya Subramanian, and Rod Russell

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May 24, 1996

DESCRIPTION OF SCIENTIFIC RESEARCH GOALS

The ***primary goals*** of our research were to obtain a fundamental understanding of the mechanisms and kinetics of shock initiated intermetallic reactions. Several issues were addressed in this study, including investigation of (i) rate-controlling parameters of shock-initiated chemical reactions, (ii) mechanisms accounting for the extraordinarily rapid kinetics associated with shock-induced reactions, and (iii) determining how the reaction mechanisms and kinetics can be controlled by altering peak shock pressure and pulse duration, powder particle morphology, volumetric distribution or reactants, and starting porosity, in systems of highly exothermic powder mixtures.

The ***overall approach*** involved investigation of shock initiated intermetallic reactions in powder mixtures of Ti-Si (titanium/silicon) and Al-hematite systems. Ti-Si is a typical intermetallic forming system having a large negative heat of reaction (ΔH_R = -138 kcal/mol) with Si exhibiting a characteristic decrease in melting temperature with increasing pressure. The aluminum-hematite mixture is a typical metal-oxide thermite system (ΔH_R = -193 kcal/mol), but can also be modified by reducing the oxide such that it contains various levels of oxygen until the composition approaches that of an Al-Fe intermetallic (H_R = -38 kcal/ mol). The main effort in this program was focused on coupling the shock-compressed reactant powder configuration just prior to reaction initiation with the propensity for reaction, via microstructural characterization (using optical metallography and x-ray diffraction analysis) of samples obtained from recovery experiments. Real-time pressure measurements using PVDF gages were also performed. The experimental results demonstrate the influence of the shock pulse duration and initial packing density in Ti-Si powders, and the role of volumetric distribution of reactants on the crush-up to solid density (and therefore the configuration of reactants prior to reaction initiation), on the propensity of reaction initiation in Al + Fe_2O_3 thermite mixtures.

The overall effort was coordinated with concurrent investigations at Washington State University (for controlled recovery experiments) and North Carolina State University (for numerical simulations). In addition, shock recovery and time-resolved measurements were also performed in collaboration with and using the gas gun facilities at Sandia National Laboratories.

INTRODUCTION AND BACKGROUND

Shock compression of reactive elemental powder mixtures can lead to chemical reaction, forming compounds and rapid increases in temperature [1,2]. The occurrence of such shock induced chemical reactions in powders is controlled by factors such as shock pressure, pulse duration, and packing density, as well as powder morphology, volumetric distribution of reactants, and the difference between the mechanical properties of the constituents [3-7]. The reactions which occur during the high pressure state have been defined as shock-induced reactions, and are believed to be controlled by mechanisms prevailing in the microsecond duration of high pressure shock state [8].

In the present study, the effect of pulse duration was investigated for the Ti-Si system using medium morphology powder. Altering the pulse duration would be expected to affect the time available for processes involved in compression of powder mixtures, which would therefore, influence the reaction behavior of the powders. Previous studies on shock-compression of Ti-Si powders have found that the threshold conditions for reaction depend on the powder morphology and packing density. Medium morphology powders appear to be most reactive, with reactions occurring at pressures as low as 1 GPa at ~53 % TMD, based on results of time-resolved and recovery experiments [6,9,10]. The shock-induced reaction behavior of Al-Fe, Al-Fe_2O_3 and Al-Fe_3O_4 powders was also investigated to examine the effect of volumetric distribution and packing density on the reaction behavior, in experiments at different shock pressures and packing density, and with powders of two different morphologies.

In the following sections, the results of the Ti-Si intermetallic and aluminum-hematite thermite system will be described seperately. The experimental procedure and conditions used will be presented first, followed by the discussion and summary of results. Final remarks summarizing the conclusions of the work will also be included.

Ti-Si INTERMETALLIC SYSTEM

EXPERIMENTAL PROCEDURE

Medium morphology polycrystalline Ti and single-crystal Si powders, similar to those used in previous studies [6,9,10], and amorphous Si powders, were mixed in 5:3 atomic ratio. The mixtures were prepared using a slow speed mechanical blender, and packed at 66%, 61%, 54%, and 43% of theoretical maximum density (TMD), in a four-cavity planar-impact copper fixture [11], shown in Figure 1. The experiments were performed using a copper flyer plate (5mm and 2.47mm thick to obtain two different pulse durations), at an impact velocity of ~0.35 km/s, with the 4" diameter gas gun at Washington State University. Optical and scanning electron microscopy were used to analyze the recovered samples. X-ray diffraction was used to identify the phases and line broadening analysis was used to calculate the residual strain in Ti, in unreacted samples. The XRD peaks were fit with a Lorentzian function to obtain peak-width at half intensity, which after subtraction of instrumental broadening was used in Williamson Hall plots to calculate the residual strain and crystallite size [12].

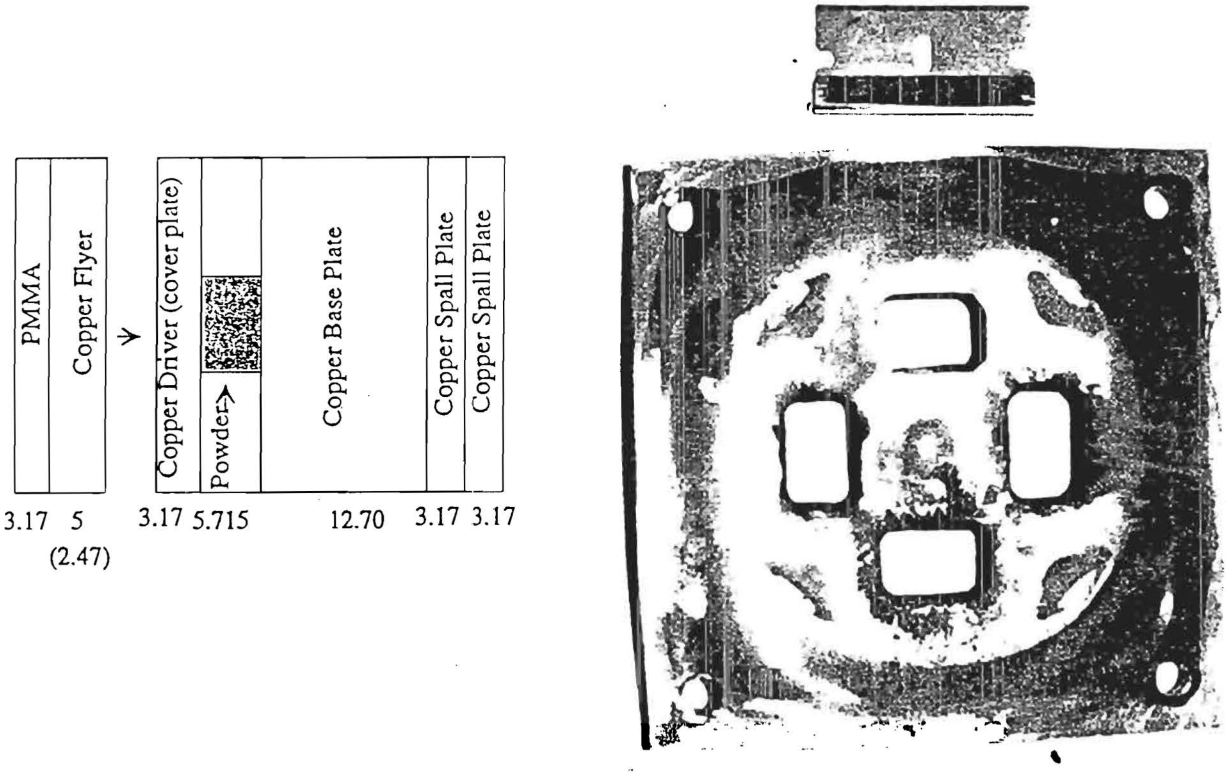

Figure 1. Components of the four-cavity fixture and phot of powders sample holding plate.

RESULTS OF EXPERIMENTS

Table I lists the experimental conditions used in the present study. Using the impedance matching technique and the calculated Hugoniot for 5Ti+3Si powder mixture an initial pressure of ~6 GPa in the copper driver and 0.7-0.85 GPa in the powder was computed. The recovered samples showed occurrence of reaction influenced by flyer thickness (pulse duration) and initial powder packing density. The reaction map for the various experiments performed, is shown in Figure 2.

TABLE I - SUMMARY OF EXPERIMENTAL RESULTS ON Ti-62.5at%-Si-37.5at%

Density (T.M.D.)	**Shot 1 (Flyer=5.03mm)**	**Shot 2 (2.47mm)**	**Shot 3 (5.03mm)**	**Shot 4* (2.47mm)**
66%	-----	unreacted	unreacted	-----
~61%	reacted**	unreacted	unreacted	-----
54%	-----	unreacted	reacted	unreacted
43%	reacted	-----	-----	reacted

* Crystalline and amorphous Si powder; **Packing error yielding density in the 50-60% TMD range

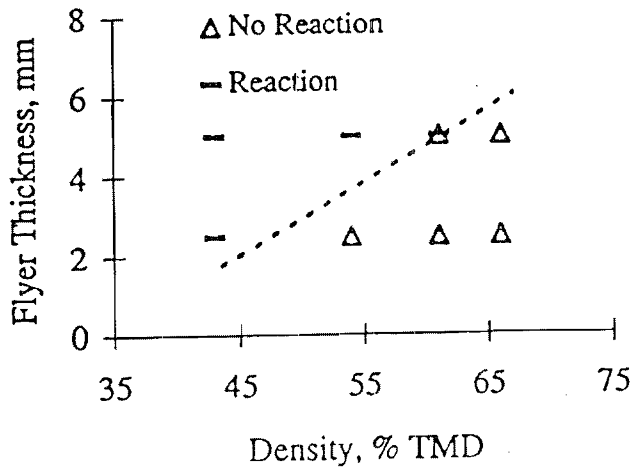

Figure 2. Reaction Map as a Function of Flyer Thickness and Initial Packing Density.

The reacted samples formed single phase Ti_5Si_3 compound with a uniform microstructure and high levels of porosity throughout the compact, as shown in Figure 3 (shot #3, 54% TMD). The lattice parameter of Ti_5Si_3 was measured and is shown in Table II. The lattice parameter did not change significantly for the Ti5Si3 reaction product formed under conditions of different densities and pulse durations.

FIGURE 3. Microstructure of fully reacted sample showing uniform microstructure and high levels of porosity. (Flyer Thickness - 5 mm, Density - 54% TMD, shot # 3).

TABLE II. LATTICE PARAMETER OF Ti_5Si_3 IN REACTED SAMPLES

Flyer Thickness	Density (%TMD)	Lattice Parameter (A) a	c
5 mm	61	7.4511	5.1502
	54	7.4588	5.1689
	43	7.4563	5.1594
2.47 mm	43(a-Si)	7.4627	5.1540
	43(x-Si)	7.4581	5.1525

The unreacted samples were comprised of deformed Ti and Si particles. Some large Si particles showed cracking. A typical microstructure of regions close to the impact, center and back surface for the unreacted Ti-Si compact is shown in Figure 4 (shot# 2, 66% TMD). No obvious variation in the deformation characteristics were observed in these micrographs. Similar results were also observed for the other unreacted compacts.

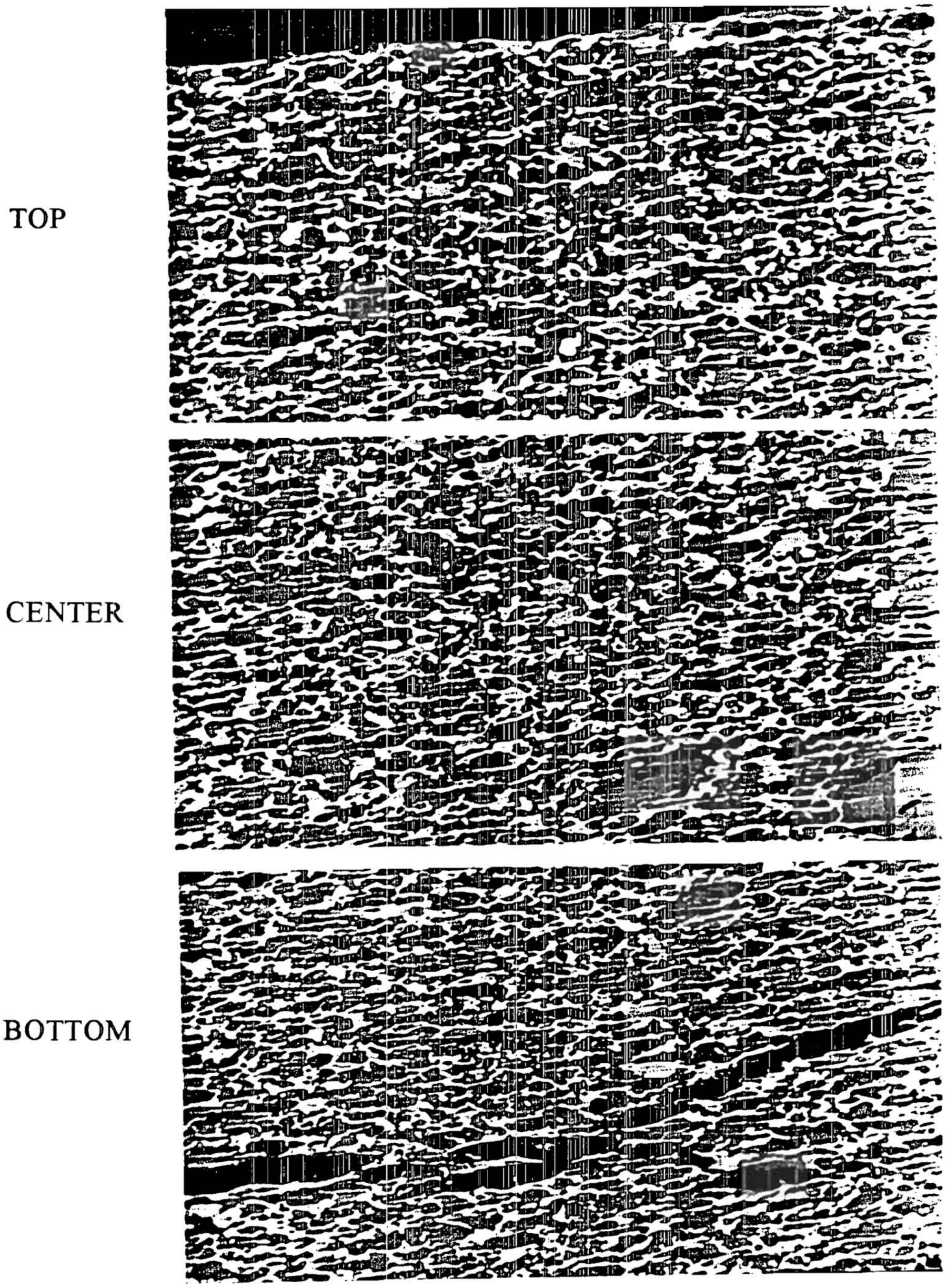

FIGURE 4. Microstructure of unreacted sample at (a) impact, (b) center, and (c) back surface showing no evident dissimilarity in deformation response as a function of compact thickness (Flyer thickness 2.47 mm, Density 66%, Shot # 2). ***{Magnification: 1 cm = 0.1 mm}***

In addition, there was no evidence of any partial reaction at regions of interparticle contacts between Ti and Si as shown in a higher magnification micrograph in Figure 5 (shot # 3, 61% TMD). Rresidual strain values in unreacted Ti are shown in Table III. No significant change in strain was observed as a function of density and pulse duration. The strain values for Ti correspond to dislocation densities of ~ 10^{11}-10^{12} cm^{-2} based on Williamson and Smallman approach [13].

FIGURE 5. Scanning Electron Micrograph of boundary region between bright Ti and dark Si powder particles revealing evidence of no interparticle reaction. (Flyer Thickness - 5 mm, Density - 61% TMD, Shot # 3).

TABLE III. RESIDUAL STRAIN IN UNREACTED Ti.

Flyer Thickness	Density (% TMD)	Strain
5 mm	66	0.0040
	61	0.0032
2.47 mm	66	0.0036
	61	0.0030
	54 (a-Si)	0.0039
	54 (x-Si)	0.0038

DISCUSSION OF RESULTS

Based on the observation of a uniform microstructure and occurrence of either complete or no reaction, it appears that the reaction in Ti-Si powder mixtures is shock induced. Once the reaction is initiated, it becomes self-sustaining and moves through the sample thickness consuming all reactants. The final reaction product is subsequently controlled by thermal effects of reaction yielding a uniform microstructure and similar lattice parameter of products. Reducing the density from 53% to 43% increases the volume of voids where mixing and flow of constituents can be attained, which results in greater propensity for reaction to occur [6]. The variation of flyer thickness combined with variations in powder packing density, results in a complex shock loading effect. The effect manifests by influencing the pulse duration, attenuation of initial pressure, and magnitude of the final peak pressure generated upon equilibration of the shock waves between the driver and backing copper plates. The actual loading histories obtained from two-dimensional numerical simulations using the AUTODYNE-2D computer code are illustrated in Table IV.

TABLE IV - LOADING HISTORIES CALCULATED USING AUTODYNE-2D

	66% dense	54% dense
2.47 mm (0.9 μs)	P_{ini} = 0.77 GPa atten: @ 1mm	P_{ini} = 0.70 GPa atten: @ 0.5mm
	2-D pressure = 1.5 GPa	
5.00 mm (1.3 μs)	P_{ini} = 0.85 GPa atten: @ 2 mm	P_{ini} = 0.75 GPa atten: @ 1 mm
	2-D pressure = 2.5 GPa	

It can be seen that the smaller flyer thickness (2.47 mm) results in an initial shock pulse of smaller duration and magnitude which attenuates within 0.5 mm of travel through the 54% dense powder and 1 mm travel through 66% dense powder, while yielding a contant peak pressure. In contrast, with the thicker flyer plate, the pulse duration and magnitude of the initial wave, as well as the peak pressure are all increased. Thus, not only is the powder loaded at higher stresses, but longer time is also available with the thicker flyer plate, which provides increased time for mechano-chemical events neccessary for reaction initiation. Hence, with the thicker flyer plate, reaction is observed with higher initial powder packing densities.

ALUMINUM-HEMATITE THERMITE SYSTEM

RECOVERY EXPERIMENTS

EXPERIMENTAL PROCEDURE

Mixtures of Al-Fe, Al-Fe_2O_3, and Al-Fe_3O_4, blended in an equivolumetric ratio were shock compressed at different packing densities and shock conditions. The shock conditions were varied by using different combinations of Sandia Bear series recovery fixtures and explosives [14,15]. The Momma Bear A fixture with Baratol explosive (MBA-B), Poppa Bear fixture with Baratol explosive (PB-B) and Momma Bear A fixture with Comp B explosive (MBA-CB) were used. The pressure and temperature obtained in these fixtures have been characterized by two-dimensional numerical simulation [15]. The peak pressure and mean bulk temperatures computed for 54% rutile powder. in the different regions of the capsule are shown in Table V. It should be noted that peak pressures generated due to radial focussing effects are independent of the equation of state of a material [15].

TABLE V. - CHARACTERISTICS OF THE BEAR FIXTURES [15]

Fixture	Pressure, GPa		Mean Bulk Temperature, K	
	Bulk	Focus	Bulk	Edge
PB-B	5	4.5	423	348
MBA-B	16	32	498	583
MBA-CB	22	46	673	923

The details of the experimental conditions of the present study are shown in Table VI. The recovered samples were characterized using optical and scanning electron microscopy. X-ray diffraction was used to analyze the phases formed and to calculate the residual strain in the unreacted powders. The peaks were fit with a Lorentzian function to obtain the peak width at half intensity, which after subtraction of instrumental broadening was used in Williamson-Hall plots (12) to obtain the residual strain values.

TABLE VI: SHOCK RECOVERY EXPERIMENTS ON Al-Fe/Fe_2O_3/Fe_3O_4

SAMPLE	SHOCK CONDITION	MIX & RATIO (vol%)	DENSITY	MORPHOLOGY (g/cm^3)	RESULTS
Alfe01	MBA-B	Al+Fe2O3	53%	fine	reacted
Alfe02	MBA-B	Al + Fe2O3	53%	coarse	reacted
Alfe03	MBA-B	Al+ Fe3O4	53%	fine	reacted
Alfe04	MBA-B	Al+ Fe3O4	53%	coarse	reacted
Alfe05	MBA-B	Al+Fe	53%	fine	not reacted
Alfe06	MBA-B	Al+Fe	53%	coarse	not reacted
Alfe01a	MBA-B	Al+ Fe2O3	70%	fine	not reacted
Alfe02a	MBA-B	Al+ Fe2O3	70%	coarse	not reacted
Alfe01asa	MBA-B	Al+ Fe2O3	70%	Sandia	not reacted
Alfe01b	PB-B	Al+ Fe2O3	53%	fine	not reacted
Alfe03b	PB-B	Al + Fe3O4	53%	fine	not reacted
Alfe01bsa	PB-B	Al+ Fe2O3	53%	Sandia	not reacted
Alfe01c	MBA-CB	Al+ Fe2O3	53%	fine	reacted
Alfe01d	MBA-CB	Al + Fe2O3	70%	fine	reacted

RESULTS AND DISCUSSION

The recovered samples showed occurrence of reaction as a function of the density and shock loading conditions. The MBA-CB (~22 GPa) configuration showed reaction for both 53% and 70% densities. The 53% density MBA-CB sample reacted in an explosive manner causing a hole to form at the top of the capsule, through which most of the sample was ejected. The MBA-B configuration showed reaction for only the 53% TMD sample. The PB-B (~5 GPa) configuration showed no reaction even for the 53% density. The cross-section of a fully reacted sample, illustrated in Figure 6, showed separation of the reaction products Al_2O_3 and FeAl (due to differences in their melting temperatures) and microstructural features of melting and solidification. Melting of the reaction products is expected since the temperature due to the reaction for the Al-Fe_2O_3 (ΔH = -3400 kJ/kg) and Al-Fe_3O_4 (ΔH = -3061 kJ/kg) compositions is 2790 K. The exothermic heat also caused discoloration of the copper capsule. The lattice parameter of the Al_2O_3 and FeAl formed due to the reaction did not change significantly for the different conditions used, as shown in Table VII.

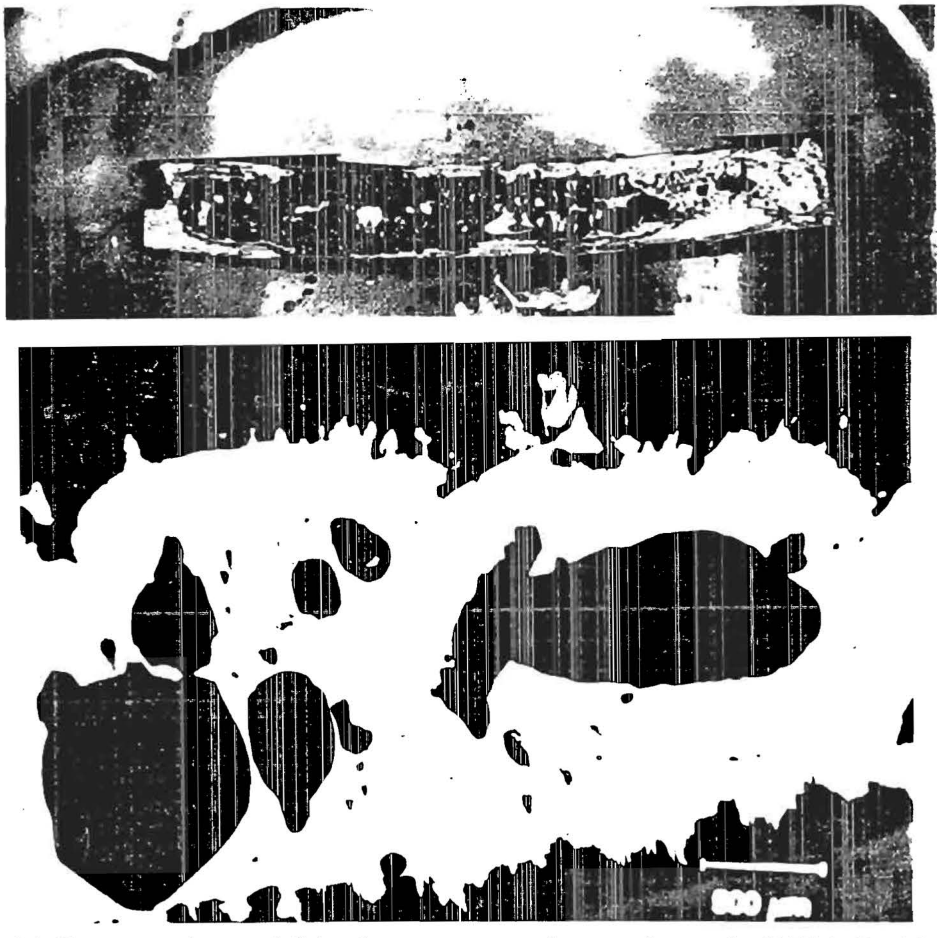

FIGURE 6. (a) Cross-section and (b) microstructure of reacted sample (MBA-B, Al+Fe_2O_3 (fine), 53% TMD) showing seperation of reacted, melted products.

TABLE VII. LATTICE PARAMETER OF REACTED SAMPLES

Fixture	Density (%TMD)	Composition (Morphology)	Lattice Parameter (A)	
			Al2O3	FeAl
MBA-B	53%	Al + Fe2O3 (fine)	a=4.761, c=13.000	a=2.8964
	53%	Al + Fe2O3 (coarse)	a=4.753, c=12.962	a=2.903
	53%	Al + Fe3O4 (fine)	a=4.767, c=12.991	a=2.8968
	53%	Al + Fe3O4 (coarse)	a=4.764, c=13.081	a=2.9203
MBA-CB	70%	Al + Fe2O3 (fine)	a=4.764, c=13.018	a=2.8966

The unreacted samples were comprised of deformed aluminum particles and fractured Fe-oxide particles, with cracks oriented in the shock direction. The microstructure of unreacted samples of fine and coarse powder mixtures are shown in Figure 7 (grey Fe_2O_3 and dark Al particles). The strain in the Fe_2O_3 powders is shown in Table VIII. The strain in Fe_2O_3 powder was slightly higher for the higher pressure MBA-B samples compared to the PB-B sample. The Al particles showed no strain due to annealing effects with shock temperature exceeding its recrystallization temperature.

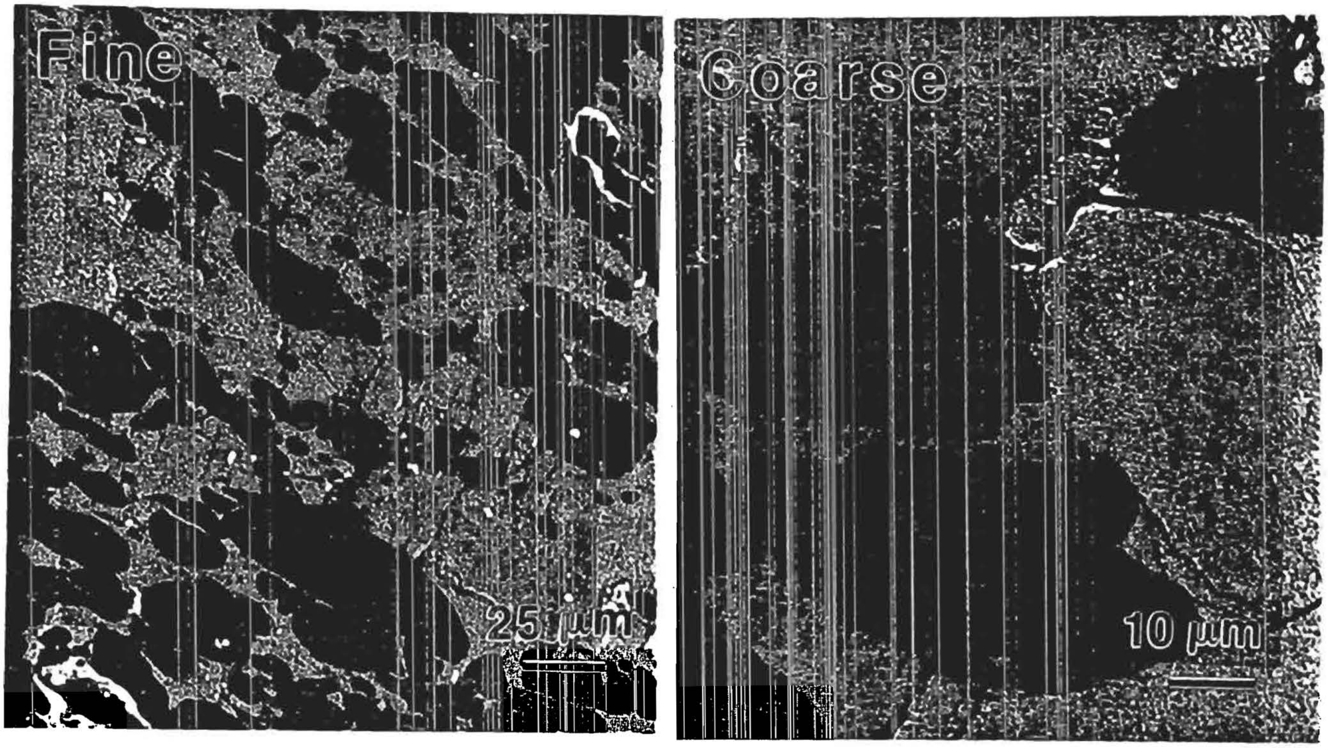

FIGURE 7. SEM micrographs of (a) fine and (b) coarse mixtures of unreacted MBA-B, Al + Fe_2O_3, 70% TMD samples.

TABLE VIII. RESIDUAL STRAIN IN UNREACTED AL + Fe_2O_3 SAMPLES

Fixture	Density (%TMD)	Morphology	Strain in Fe_2O_3
MBA-B	70%	Fine	0.0071
	70%	Coarse	0.0066
	70%	Fine*	0.0075
PB-B	53%	Fine	0.0041
	53%	Fine*	0.0050

*Same powders as those used in Sandia Experiments

The overall results of experiments performed on Al-Fe_2O_3 powder mixtures are summarized in the reaction map, shown in Figure 8, as a plot of pressure and packing density. The peak pressures were based on the values obtained for 53% dense rutile powder by two dimensional numerical simulation [15]. It can be noted from Figure 8 that for packing densities of 53% TMD, reactions are observed at pressures greater than 16 GPa. With increase in packing density to 70% TMD, an even higher shock pressure is required (22 GPa). This is expected since lower densities provide increased volume of voids, which permit better flow and mixing of the constituents. In addition, the residual temperatures attained upon equilibrium are also higher at lower densities.

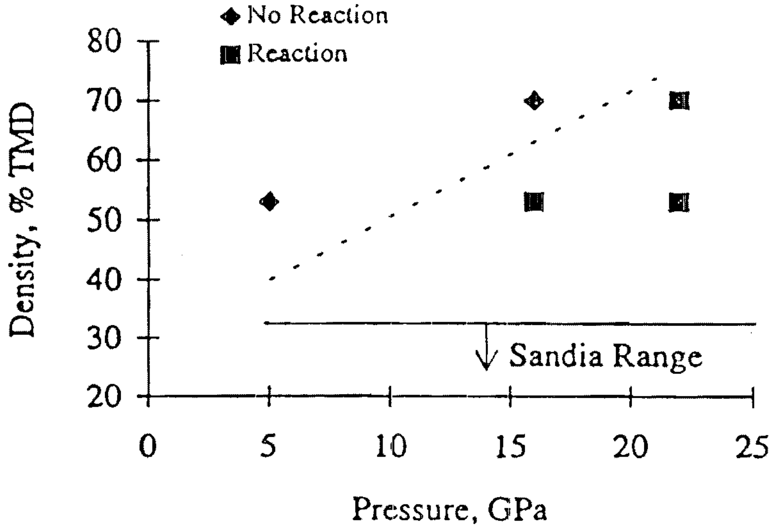

FIGURE 8. Reaction Map for Al + Fe2O3 (fine) as a function of pressure and density.

The results of the present experiments performed on non-stoichiometric but equivolumetric mixtures were compared with experiments on stoichiometric Al-Fe_2O_3 (2:1 atomic ratio) done at Sandia National Laboratories with even lower densities (<35% TMD) using MBA-CB and MBA-B fixtures [15]. The range of densities in their experiments is also shown in Figure 8. It is interesting to note that although the densities of the Sandia experiments were lower than those used in the present study, for similar values of pressure, some of their samples did not react. The Sandia experiments were performed on stoichiometric mixture of Al-Fe_2O_3 in contrast to the equivolumetric mixtures used in the present work. This suggests that the volumetric distribution of the constituents, is another experimental parameter controlling the reaction behavior. The stoichiometric composition corresponding to Al-Fe_2O_3, represents a 2:3 volumetric ratio of Al and Fe_2O_3 powders. Thus with excess Fe_2O_3 on a volumetric scale, the flow and deformation during shock compression of the Sandia mixtures, may be restricted, which can inhibit the reaction. The results of the present study, showing that equivolumetric distribution of reactants increases the reactivity of powder mixtures, were re-investigated using time-resolved pressure measurements to determine the influence of volumetric distribution on their compressibility characteristics.

TIME-RESOLVED EXPERIMENTS ON 53% DENSE Al-Fe_2O_3 MIXTURES

Time resolved pressure measurements were performed on Al + Fe_2O_3 powder mixtures using PVDF gages, to determine the differences in the shock compression response of powders mixed in different volumetric distributions. The experiments performed were essentially an extension of the earlier results documented by Holman et al [16], in which the compressibility of the powder mixture was found to be dominated by the varying compressibility of individual reactants at different stress levels. Thus, at lower stresses the compressibility was dominated by Al, and at higher stresses (upto the crush strength), the compressibility was dominated by Fe_2O_3 [16].

The PVDF gauge stress-wave measurements were performed using the 25 mm single-stage compressed-gas gun at Sandia National Laboratories. This gun is precisely controlled in velocity, planarity, and tilt, and the symmetric impact of flyer plate and target materials provides a controlled shock-compression of the target. The powder-mixtures were pressed directly into the copper capsules with PVDF gauge packages placed in intimate contact with powder (at opposite surfaces), to monitor both **input-shock** and **propagated-shock** wave characteristics. The individual capsules were placed on the impact surface of the gun, in which a smooth-bored projectile with a 10 mm thick copper flyer plate was accelerated to a pre-selected impact velocity. A schematic of the target assembly is shown in the schematic in Figure 9 (a). Typical traces of the gauge output in current versus time and the integrated traces of stress versus time for gauge packages located at both **input-shock** and **propagated-shock** locations are also shown in Figure 9 (b) - (e). The actual sample assemblies consisted of several configurations, in order to match the impedance more closely with the powder-mixture impedance, and delay the re-shock of powder mixture to clearly detect shock-compression features. The gages used were of high quality, biaxially stretched PVDF film, poled using Bauer process to a 9.2 $\mu C/cm^2$ remnant polarization, having identical gold over platinum electrodes [17]. As shown in Figure 9 (a), the shock wave produced upon impact enters the capsule from the left and propagates through the powder sample with PVDF gauge packages monitoring the **input-shock** and **propagated-shock** wave profiles, and identifying the transit time between the two gage locations. The input PVDF gage generates a piezoelectric current as the shock wave transits the gage, with a rise time less than the shock transit time through the 25 μm film thickness. The input shock propagates through the Kel-F (or PMMA) insulation film to the insulation-sample powder mixture boundary, where a reflection is caused due to impedance mis-match. The reflected release wave then arrives back at the input PVDF gauge ~40 ns after the initial input shock as shown in Figure 9 (b). The piezoelectric current is recorded with two complementary amplifier sensitivities connected to a current viewing resistor at the PVDF gage. The combined recordings provide a high resolution current-versus-time profile which is numerically integrated to stress-versus-time (Fig. 9(d)) using the PVDFSTRESS computer code [18]. The shock wave after passing through the ~4 mm thick powder, arrives as a dispersed wave at the **propagated-shock** PVDF gage location, and generates a piezoelectric current with shock rise time altered by an order of magnitude from that recorded by the input gage, as shown in Fig. 9 (c) and the resulting stress-versus-time profile in Fig. 9 (e). All experiments were designed such that a planar shock wave propagates through the powder thickness without attenuation. Table IX lists the experiments performed on aluminum-hematite mixtures prepared with different volumetric distributions, along with the corresponding configurations.

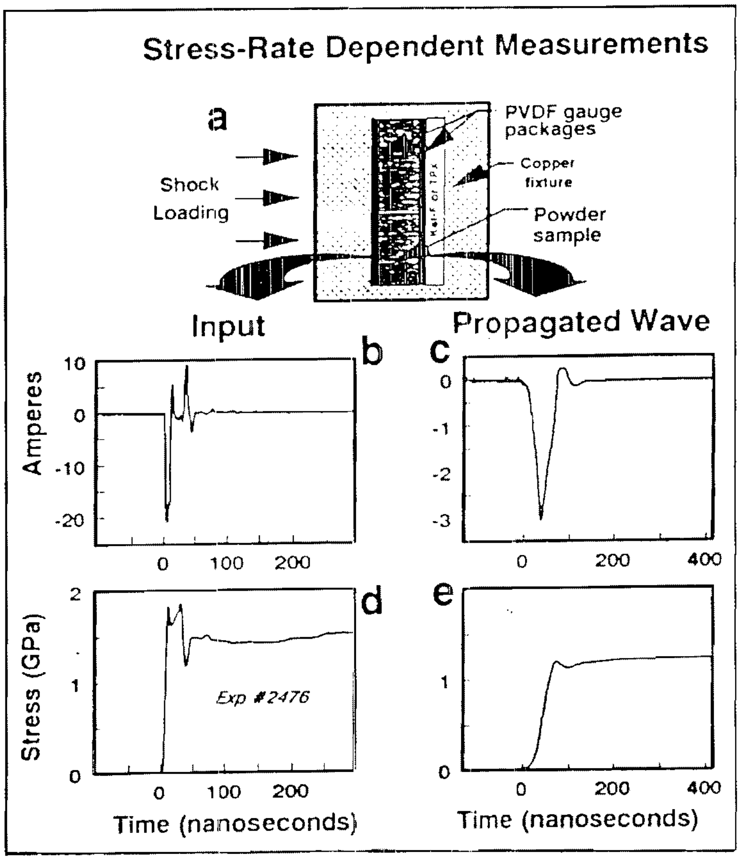

FIGURE 9. (a) Typical configuration for time-resolved experiments showing powder mixtures encased in copper capsule, with PVDF stress gauges and polymer backing at input and propagated shock locations in direct contact with powders. (b) and (c) characteristic current pulses generated by the piezoelectric PVDF gauges, measuring wave velocity and stresses at input and propagated shock locations; (d) and (e) Corresponding stress profiles at input and propagated gage locations.

TABLE IX - TIME-RESOLVED EXPERIMENTS ON 53% DENSE ALUMINUM-HEMATITE MIXTURES

Exp. # *	Mol Ratio		Volume Ratio, %		Density gm/cm^3	Proj. Velocity min/usec	Measured Input Stress GPa	Wave Speed mm/usec		Propagated Waveform Stress GPa	Relative Volume		Risetime (ns)	
	Al	Fe_2O_3	Al	Fe_2O_3				toe-toe	half max		toe-toe	half max	toe-toe	10-90%
2627 B (4.117)	1	1	24.7	75.3	2.418	0.2336	0.4	0.778	0.760	0.408	1.377	1.351	330	180
2628 B (4.094)	1	1	24.7	75.3	2.409	0.5917	1.73	1.43	1.414	1.7	1.273	1.259	90	40
2485 A (4.191)	2	1	39.8	60.4	2.219	0.3144	0.67	1.05	1.038	0.97	1.385	1.372	310	160
2484 A (4.166)	2	1	39.6	60.4	2.250	0.6347	1.94	1.8	1.77	2.82	1.377	1.362	140	100
2629 B (4.114)	3.05	1	50	50	2.065	0.5463	1.41	1.24	1.16	1.61	0.9474	0.8122	560	240

Notes: *A and B refer to experimental configuration, where A corresponds to KEL-F backing and use of 0.0005" thick teflon film on either side of each gage package, and B corresponds to PMMA backing and 0.001" teflon on either side of gage package; Number in parantheses is sample thickness in mm. Experiments 2484 2485 represent stoichiometric Al+Fe_2O_3 mixtures of Holman et al's [ ] study.

The **projectile velocity** data obtained in the experiments, correspond to highly accurate values obtained with the controlled design and set-up of the gas gun and precise velocity measurement capabilities. The **measured input stress** shown in the Table, corresponds to the stress in the powder, measured by the **input-shock** gauge. The wave speed is the wave velocity through the powder, obtained by measuring transit time between the two gauges placed in direct contact with opposite surfaces of powder compact (less insulation between powder and gauge). The **propagated waveform stress**, measured by the **propagated-shock** gage placed between the powder and polymer backing material, corresponds to the stress resulting from the interaction between the powder mixture and the polymer backing. The **relative volume** of sample is calculated from values of known initial density, measured mean input stress and wave velocity, and jump conditions for conservation of mass and momentum. In reality, the stress pulses propagating through ~4 mm thick powder mixtures, reveal a structure characteristic of wave dispersion effects, with **shock rise times** greater than hundred nanoseconds [16]. With such wave dispersion effects, the calculation of the **relative volume** based on jump conditions applied to a steady-state shock wave, may not be appropriate. One can, however, use the *calculated* **relative volume** along with *measured* **input stress** to obtain first-order powder-compressibility effects.

The *measured* **input stress** plotted as a function of the *calculated* **relative volume**, to obtain compressibility characteristics of Al-Fe_2O_3 powder mixtures of the different volumetric distributions is shown in Figure 10. The solid density curve is indicated as the vertical line passing through the theoretical density of the fully dense mechanical mixture of Al and Fe_2O_3. Points corresponding to experimentally *measured* **input stress** and *calculated* **relative volume** for the three different volumetric distributions show different compressibility trends. It can be seen that the one dat point for 50:50 vol% mixture indicates crush-up to full density occurring at pressures much lower than that for the 25:75 vol% and 40:60 vol% mixtures. Although the result corresponds to only one data point for the 50:50 vol% mixture and an overall scenario which does not reveal a clear trend of the influence of volumetric distribution on crush up to solid density, the result shows a significant effect, which can explain the different reaction thresholds observed between the equivolumetric (50:50 vol%) and equi-stoichiometric (40:60 vol%) powder mixtures in recovery experiments. Additional experiments are currently underway to obtain more data points to confirm the overall effect.

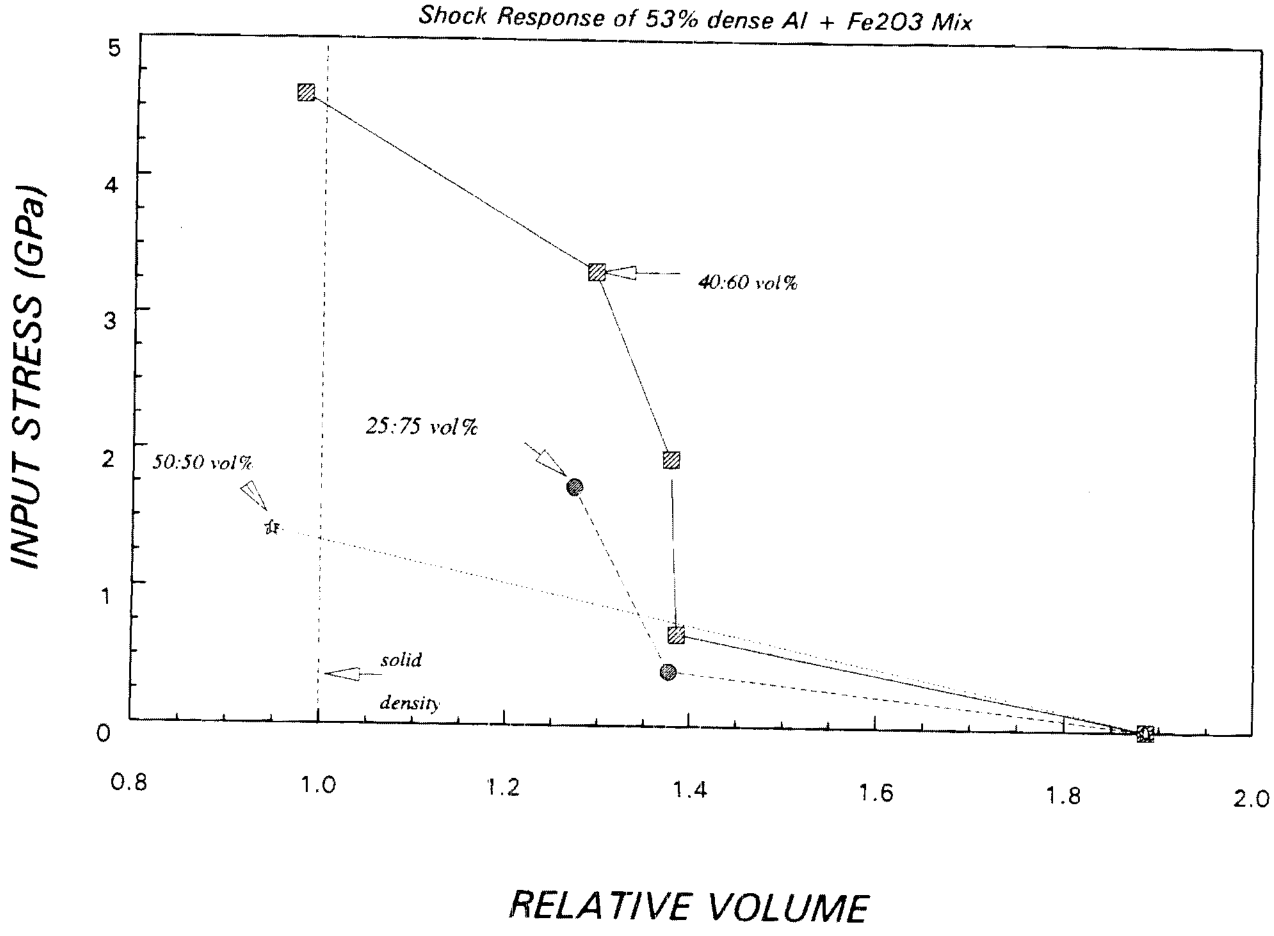

FIGURE 10: *Measured* **input stress** plotted as a function of *calculated* **relative volume**, to obtain compressibility characteristics of Al-Fe_2O_3 powder mixtures of the different volumetric distributions.

Differences in the compressibility characteristics can also be clearly observed from comparison of the raw data of current-versus-time and the corresponding stress-versus-time traces of the propagated (backer) gage, shown in Figure 11 (a) and (b), respectively. It is interesting to note from the stress-versus-time traces that with the 50:50 vol% mixture, the input stress of 14.1 kbar magnitude results in increasing the rise time of the propagated wave to 240 ns, which appears to be the cause of the significant lowering of the crush-up characteristic of this powder mixture, in contrast to the other off-volumetric mixtures.

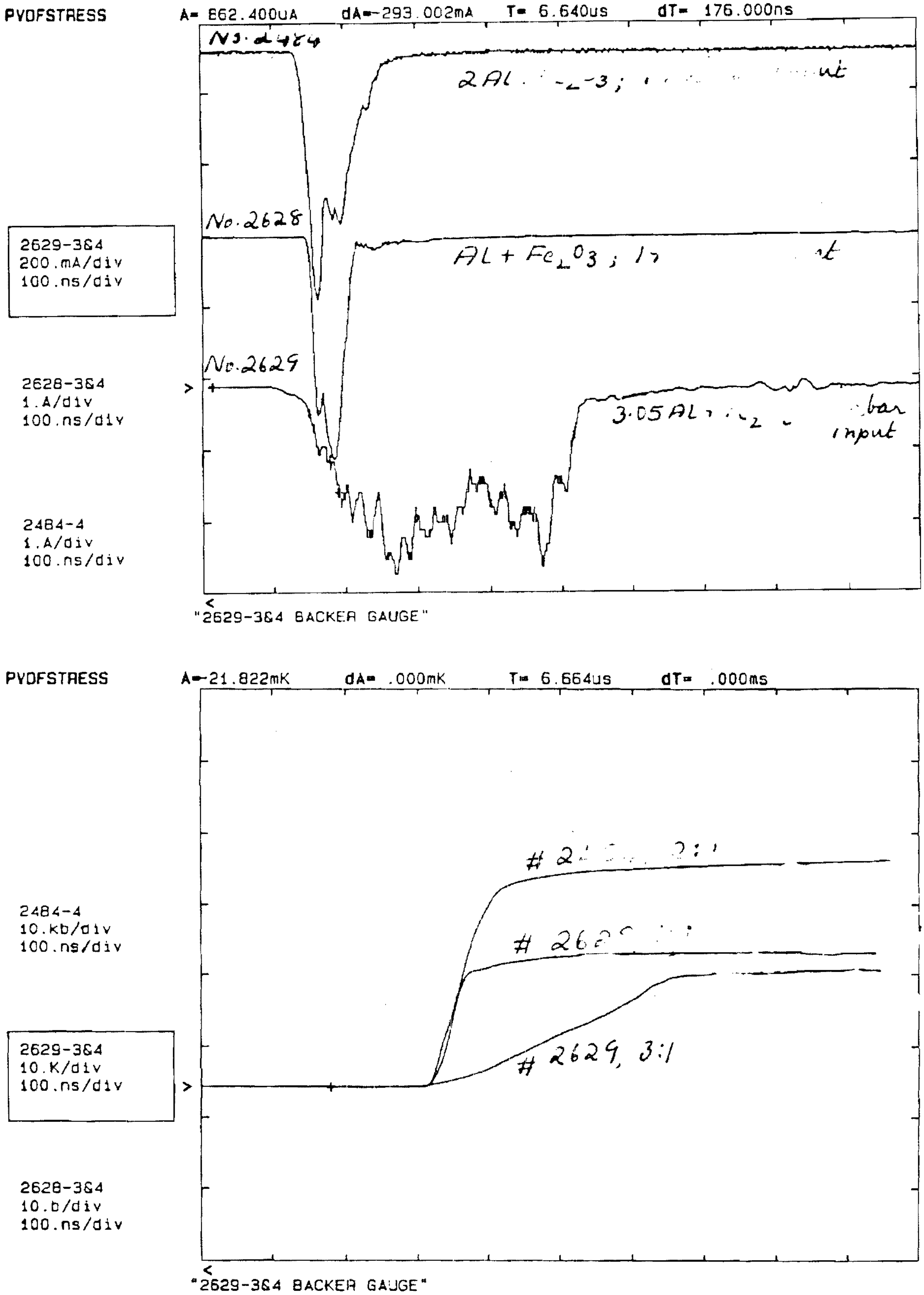

FIGURE 11. (a) Measured traces of current-versus-time and (b) integrated traces of stress-versus-time for Al-Fe_2O_3 powders mixed in different volumetric ratios and shock-compressed at initial stress magnitudes of 14-19 kbars.

CONCLUSIONS

Shock compression of Ti and Si powder mixtures resulted in chemical reaction, leading to the formation of Ti_5Si_3 intermetallic. The unreacted samples obtained due to loading with higher packing density or smaller pulse duration were comprised of deformed Ti and Si reactants, uniformly distributed through the sample cross-section. The results of this study showed an important effect of the duration and amplitude of the initial shock pulse on the propensity for reaction in Ti-Si powder mixtures.

In Al and iron oxide powder mixtures (equivolumetric), it was observed that reaction between two constituents takes place depending on the initial powder packing density and shock conditions. The reaction product underwent melting and solidification, forming an intermetallic core and an aluminum oxide layer surrounding it. The unreacted samples were comprised of deformed aluminum and fractured iron oxide particles. Comparing these results with the Sandia experiments on stoichiometric composition, it was observed that the volumetric distribution of the components is an important experimental factor influencing the reactivity of mixtures under shock compression. An equivolumetric distribution allows for better mixing between reactants and thus enhances the propensity for reaction initiation. Time-resolved pressure measurements confirmed that during shock compression, equivolumetric powder mixture crush-up to solid density at much lower stresses than Al-rich or Al- deficient Al-hematite powder mixtures, suggesting that lowering of the crush-strength is a means to increase the propensity of shock-induced reactions in powder mixtures.

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
01 November 1993 through 31 May 1996

R&T Number: 33e1852

Contract/Grant Title: N00014-9410169

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a. Number of Papers Submitted to Referred Journal but not yet published: none

b. Number of Papers Published in Referred Journals: (List Attached): none

c. Number of Books or Chapters Submitted but not yet Published: none

d. Number of Books or Chapters Published (List Attached): none

e. Number of Printed Technical Reports & Non-Referred Papers (List Attached): 2

f. Number of Patents Filed: none

g. Number of Patents Granted (List Attached): none

h. Number of Invited Presentations at Workshops or Professional Society Meeting (List Attached): 1

i. Number of Presentations at Workshops or Professional Society Meetings (List Attached): 1

j. Honors/Awards/Prizes for Contract/Grant Employees: (List Attached, may include Society Awards/Offices, Promotions, Faculty Awards/Offices, etc. none

k. Providing the following information will assist with statistical purposes.

PI/CO-PI:	TOTAL	1	Grad Students:	**TOTAL	0
	Female	0	Female		
	Minority*	0	Minority*		
Undergraduate students:	TOTAL	2	Post Doc:**	TOTAL	1
	Female		Female		1
	Minority		Minority*		

l. Degree Granted (List Attached): none

* Under-represented or minority groups include Blacks, Hispanics, and Native Americans. Asians are not considered an under-represented or minority group in science and engineering.

** Supported at least 25% this year on contract/grant.

Enclosure (2)

LIST OR PUBLICATIONS/REPORTS/PATENTS/GRADUATES *

1. Papers Published in Referred Journals:

   - none -

2. Books (and sections thereof) Published:

   - none -

3. Technical Report, Non-Refereed Papers:

   (1) V. SUBRAMANIAN and N.N. THADHANI, "Reaction behavior of Shock-Compressed Al and Fe-Oxide Powder Mixtures," to be published in Shock Compression of Condensed Matter, ed. S.C. Schmidt, 1995.

   (2) N.N. THADHANI, V. SUBRAMANIAN, R. RUSSELL, D. SAVAGE, and Y.M. GUPTA, "The Influence of Pulse Duration on Shock-induced Chemical Reaction in Ti-Si Powder Mixtures," to be published in Shock Compression of Condensed Matter, ed. S.C. Schmidt, 1995.

4. Presentations:

   (1) V. SUBRAMANIAN, "Reaction behavior of Shock-Compressed Al and Fe-Oxide Powder Mixtures," presented at the APS Topical Conference on Shock Compression of Condensed Matter, Seattle, 13-18 August, 1995.

   (2) N.N. THADHANI, "The Influence of Pulse Duration on Shock-induced Chemical Reaction in Ti-Si Powder Mixtures," presented at the APS Topical Conference on Shock Compression of Condensed Matter, Seattle, 13-18 August, 1995.

5. Patents Granted:

   - none -

6. Degrees Granted (name, date, degree):

   - none -

* List only those funded directly from ONR grant/contract.

Enclosure (3)

E-18-692 N/A

1498 TITLE: (u) Controlled Shock-Initiation of Intermetallic Reactions

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FUNDING AGENCY: Office of Naval Research

R&T PROJECT CODE: 33e1852---01
CONTRACT NO: N000149410169

CURRENT END DATE: 31 MAY 1996

SCIENTIFIC OFFICER: Judah M. Goldwasser

1498 Technical Objective:

The objectives of this research are to provide an understanding of the reaction mechanisms, kinetics, and energy release characteristics of shock initiated intermetallic reactions. Issues to be addressed include: (i) accounting for the extraordinarily rapid kinetics associated with shock induced reactions; (ii) determining whether shock-induced reaction mechanisms differ from processes involving conventional nucleation and growth from the melt or solid state; (iii) determining whether shock induced plastic flow can cause restructuring of atomic arrangements to accelerate mass transport and promote rapid reaction rates; and (iv) determining how the reaction mechanisms and kinetics can be controlled by altering shock compression conditions (peak pressure and pulse duration), reactive powder material characteristics (particle morphology, volumetric distribution, and starting porosity), and the use of inert and reactive additives.

1498 Approach:

Shock initiated intermetallic reactions were investigated in powder mixtures of two main systems of study: Ti-Si (titanium/silicon) and Al-Fe/Fe2O3 (aluminum/ferric oxide) powder mixtures. Ti-Si is a typical intermetallic system having a large negative heat of reaction (HR = -138 kcal/mol) with Si exhibiting a characteristic decrease in melting temperature with increasing pressure. The Al-Fe2O3 mixture is a typical metal-oxide thermite system (HR = -193 kcal/mol), but can also be modified by reducing the oxide such that it contains various levels of oxygen until the composition approaches that of an Al-Fe intermetallic (HR = -38 kcal/ mol). The overall effort will be focused on coupling the microstructure of the shock-compressed reactant powder configuration just prior to reaction initiation with the propensity for reaction using recovery experiments. Real-time pressure measurements will also be performed to deduce the reaction kinetics. This effort will be coordinated with concurrent investigations at Washington State University and North Carolina State University. Analysis of material configuration in terms of particle size, morphology, pore size, and mixing will be conducted at Georgia Tech. Controlled one-dimensional recovery and time-resolved experiments will be designed and conducted at Washington State. Modeling of reaction kinetics, product formation characteristics, and reaction energetics will be performed at North Carolina State. Some of shock recovery experiments and all of the post-shock material characterization will be conducted at Georgia Tech. Detailed microstructural analysis will be conducted via optical metallography, scanning electron microscopy, transmission electron microscopy, and x-ray diffraction.

The shock experiments will be performed at and below threshold pressures and varying shock pulse durations in order to obtain samples with unreacted, partially reacted and fully reacted microstructures. In the Al+Fe/Fe2O3 system, modifications to the system will be made by substituting various amounts of the iron oxide with iron, which is more deformable (without fracture) than iron oxide. This will enable examination of the role of deformation and fracture characteristics of reactants on mixing and subsequent reaction. The Ti-Si system, will be used primarily to investigate the effect of shock pulse duration. In both systems, the packing density will also be varied to deduce the effects of initial porosity on the reaction response.

1498 <u>Progress</u>:

In work conducted to date, four shock recovery experiments have been performed on **Ti-Si powder mixtures**, using a four-cavity (rectangular) recovery fixture with the gas gun at Washington State University to investigate the effect of shock pulse duration. Experiments were conducted at constant impact velocity (~335 m/s), using 2.47 mm and 5.0 mm thick flyer plates to generate shock pressure pulses of two different durations. The powder mixtures were packed at initial densities of 43%, 54%, 60%, and 66% TMD. General results of the reaction response are listed in the table below. Evidence of reaction was clearly obtained by macro-observation of the recovered compacts which showed presence of large number of spherical voids in the spongy aggregate. Microstructural analysis was used to confirm the formation of reaction products, based on optical microscopy and x-ray diffraction.

SUMMARY OF EXPERIMENTAL RESULTS ON Ti-62.5at%-Si-37.5at%

Density (T.M.D.)	**Shot 1 (5.03mm flyer)**	**Shot 2 (2.47mm flyer)**	**Shot 3 (5.03mm flyer)**	**Shot 4 (2.47mm flyer)**
66%	-----	unreacted	unreacted	-----
61%	reacted*	unreacted	unreacted	-----
54%	-----	unreacted	reacted	unreacted
43%	reacted	-----	-----	reacted

*Powder packing error may yield density different from desired 61% TMD value.

The results tabulated above showed that with the impact conditions used, chemical reaction were only observed with powders packed at densities less than 61% TMD, irrespective of flyer plate thickness (and resulting pulse duration). The 61% density sample of Shot 1, was erroneously packed, so actual density value is not known. The pulse duration effect was more dominantly revealed in the case of powders packed at lower densities. Thus, while reactions were observed in powders packed at 54% density, with 5.03 mm thick flyer plate (larger duration) experiments, the 2.47 mm thick flyer (lower duration) experiment showed no reaction. On the other hand, with 43% packing density, both 5.03 and 2.47 mm thick flyer (and corresponding durations) experiments showed reaction.

The effect of pulse duration and packing density indicates that for chemical reactions to occur during shock-compression of powders, a threshold pulse duration of the peak pressure is required. Furthermore, the shock pressures employed in the experiments were significantly below the conditions that would be required to melt either of the reactants. These results suggest that shock-induced reactions in Ti-Si powder mixtures occur in time scales of the high pressure shock state via solid-state mechanisms .

Twelve experiments were also performed on **metal (Al) and oxide (of Fe) powder mixtures**. The highly exothermic nature of metal-oxide thermite mixtures and the low melt temperature of Al, causes post-shock combustion-type reactions to be easily initiated in powders packed at low densities. The Sandia Bear fixtures were used for this system to attain powder packing densities greater than 65% TMD. The results indicated that while no shock-induced reactions occurred in metal-oxide powders at densities greater than 65% TMD, post-shock combustion-type reactions always occurred in <65% density samples. Occurrence of reaction in these low packing-density samples left behind a thermal signature (ring-like pattern) in the copper capsules which indicated initiation of reaction from outside regions where temperatures exceed melt temperature of Al (determined by numerical simulations). In contrast, when higher pressures were used, shock-induced reactions were observed with thermal signatures along the axial high-pressure (but lower temperature) regions of the capsules. Experiments on the less exothermic Al-Fe powder mixtures substantiated the effect of melting of Al in low packing-density samples. While clear melting of Al was observed along outside peripheral regions of these Al-Fe compacts (in lower pressure experiments), there was no evidence of reaction due to the lower exothermicity of Al-Fe mixture. Unreacted shocked samples are now being microstructurally characterized to determine the extent of mixing via plastic deformation, particle fracture, and melting of one or both reactants due to shock compression at conditions below the reaction threshold.

SUMMARY OF PROGRESS

In an effort to understand the kinetics of shock-initiated intermetallic reactions and the process mechanisms which enable control of these reactions, recovery experiments on Ti-Si and Al-Fe/Fe203 powders were performed to determine the effect of two important variables: initial packing density (or porosity) and shock-pressure pulse duration. In the Ti-Si system, a threshold pulse duration for reaction initiation was established for constant peak pressure and initial porosity. The existence of a threshold pulse duration and the fact that reactions are initiated at conditions significantly below melting of either constituents, suggests that intermetallic reactions occur in the high-pressure shock-state via solid-state processes. Reactions in Al-Fe/Fe2O3 mixtures are complicated by the low melt temperature of Al and very high exothermicity of the system. Thus, both "shock-induced" (during shock pressure state) and "shock-assisted" (during temperature equilibration but after pressure unloading) reactions are observed in these powders.

PUBLICATIONS:

(1) V. SUBRAMANIAN and N.N. THADHANI, "Reaction behavior of Shock-Compressed Al and Fe-Oxide Powder Mixtures," to be presented at the APS Topical Conference on shock compression of condensed matter, Seattle, 13-18 August, 1995.

(2) N.N. THADHANI, V. SUBRAMANIAN, R. RUSSELL, D. SAVAGE, and Y.M. GUPTA, "The Influence of Pulse Duration on Shock-induced Chemical Reaction in Ti-Si Powder Mixtures," to be presented at the APS Topical Conference on shock compression of condensed matter, Seattle, 13-18 August, 1995.