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SHOCK-INDUCED SOLID-STATE CHEMICAL REACTIVITY STUDIES USING TIME-RESOLVED RADIATION PYROMETRY

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ABSTRACT

Time-resolved radiation pyrometry has been used to study materials which undergo solid-state chemical reactions due to shock loading. Shock-induced chemical reactivity in solids is fundamentally different than that in high explosives and other energetic materials because, if no volatiles are present, the reaction products end up in the condensed, rather than the vapor, state. Bulk property changes accompanying the solid-state reactions may therefore be too small to be observable with wave profile or shock-velocity measurements. However, some solid-state reactions, such as that between metallic nickel and aluminum, are exothermic enough to give rise to a measurable increase in temperature, so pyrometry can be used to detect the reactions. Unfortunately, these measurements are complicated by the large temperature increases generated by other sources. Possible mechanisms for generation of these high temperatures, and their effect on the chemical reaction, are suggested.

INTRODUCTION

The triggering of solid state chemical reactions by the passage of strong shock waves has been the subject of many studies. There are two main reasons for the increasing interest in shock-induced solid state reactions: 1) By studying chemical effects, our understanding of the fundamental science of the shock process should improve; 2) Shock-chemistry holds the potential to generate new or radically modified materials which might have physically interesting or technologically useful properties. Several recent studies have made use of controlled explosive loading fixtures (Graham and Webb, 1984, 1986) to shock metal and inorganic powder mixtures to well-defined pressure and mean-bulk temperature states. Recovered samples have been subjected to sophisticated analysis such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), differential thermal analysis (DTA), Mössbauer spectroscopy, x-ray diffraction and magnetometry. This post-shock analysis has demonstrated that, for example, nickel aluminides and titanium aluminides can be generated by shocking mechanical and composite mixtures of their respective component metals (Horie, Graham and Simonsen, 1985; Pak, Horie and Graham, 1986; Horie, Hoy, Simonsen, Graham, and Morosin, 1986). The issue which these studies do not address is: at what stage of the process does the chemistry occur? In order to answer this question, "real-time" measurements must be made while the sample is undergoing the shock loading and unloading process.

Radiation pyrometry is a real-time technique which lends itself to shock-induced chemical reaction studies by measuring temperature. Chemical reactions, like polymorphic phase transformations, can involve large endothermic or exothermic energies which can manifest themselves in significant, measurable temperature changes. Despite the large temperature change, the bulk properties (such as density and sound speed) of the product (or final phase) may differ little from those of the reactants (or initial phase). These bulk properties may therefore be difficult to measure with methods such as wave profile or shock-velocity experiments, and the chemical reaction or phase transformation will go undetected. This was found, for example, to be the case for the melting of stishovite by Lyzenga, Ahrens and Mitchell (1983), who observed a large temperature drop along the Hugoniot of quartz in a region with no obvious bulk property changes.

Shock induced chemical reactions do not, in general, have only a small effect on bulk properties. An extreme example of chemical reaction with large bulk property change would be high explosive detonation, in which a change of physical state (solid to vapor) accompanies the chemical reaction. This type of reaction is obviously observable with bulk property measurements. We are concerned, however, with solid state chemical reactions in which both the reactant and product are condensed matter, as in the case of the intermetallic reactions as observed in recovery experiments.

Boslough and Graham (1985) and Boslough, Graham and Webb (1986) were the first to apply radiation pyrometry to the study of the intermetallic nickel-aluminum reaction. They observed extremely large values of spectral radiance for visible and near-infrared light emitted from shocked compacts of nickel-aluminum powder mixtures. The high temperatures implied by these spectral radiance values were interpreted as being due to the large exothermic energy release of the shock-induced intermetallic reaction previously observed in recovery experiments. There were several potential problems with that interpretation, however, and the present study was intended to resolve them.

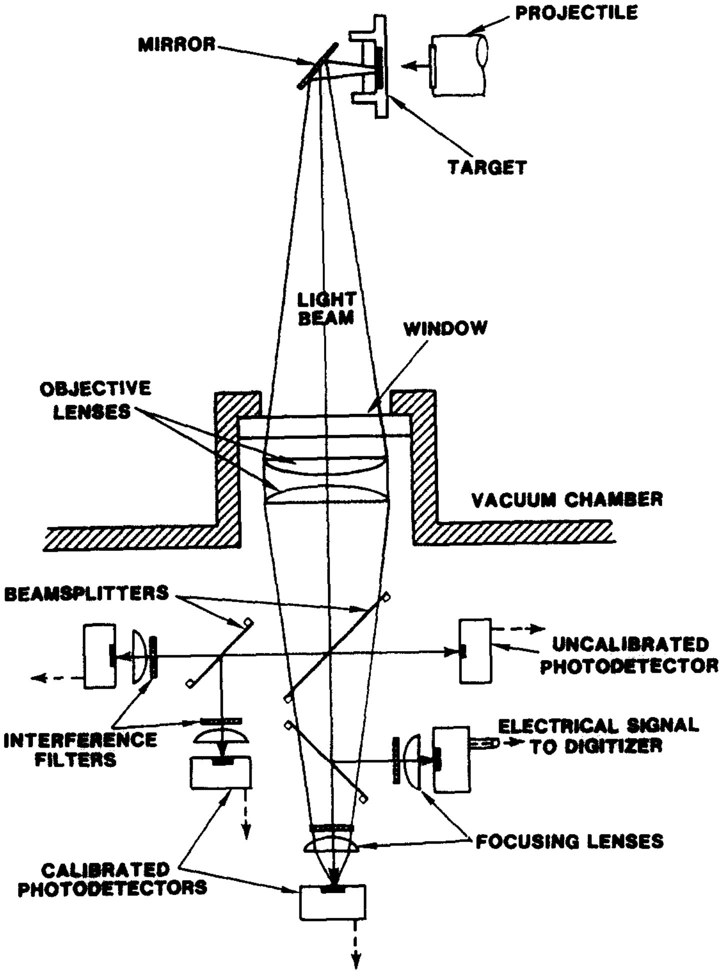

Fig. 1. Schematic diagram of radiation pyrometer and its relation to gas-gun•impact chamber

In the earlier experiments, the targets were modified explosive loading fixtures. That configuration was useful for comparing time-resolved data to the results of the recovery experiments, but the targets were not designed to constrain the observed region to one-dimensional flow as is usually the case for real-time shock wave experiments. Thus, at any given time a large range of material states (pressures and temperatures) were observed by the pyrometer. The distribution of temperatures complicates the interpretation of the data from the pyrometer, which is ideally intended to observe only one temperature at a given instant. The distribution in pressures makes it impossible to assign an observation to a particular shock state. Also, there was no way of precisely controlling the gas present in the pores of the sample compact. Spurious light from trapped air undergoing shock, or from oxidation reaction was therefore a concern. In addition, there was some evidence for light emission from the shocked sapphire window, which could lead to problems. Finally, there was no test in the earlier studies of the possibility that the high temperatures were due to physical processes, such as localized heating due to plastic deformation or pore collapse.

EXPERIMENTAL

The present experiments were carried out with a radiation pyrometer of the type described by Boslough and Ahrens (1986) and depicted schematically in Fig. 1. Absolute light intensity (spectral radiance) is simultaneously measured as a function of time at four wavelengths between .5 and 1.8 µm in the visible and near-infrared using large aperture silicon and germanium photodiodes. The signals are recorded with an array of Tektronix 7612 digitizers with a sampling rate of 5 ns. The pyrometer is calibrated prior to each experiment with a tungsten filament spectral irradiance source. By using large apertures at the target (up to 2.54 cm) and large bandwidth interference filters (up to 0.2 µm half-height full-width), the sensitivity of the system is maximized. A least squares fit to these data determines a time-resolved temperature and effective emissivity (Boslough and Ahrens, 1986). A fifth photodiode provides a faster time response to ensure that any high frequency component of light is recorded. It is a silicon avalanche photodiode with a nominal rise time of 2 ns and its signal is recorded using a Tektronix 7912 digital oscilloscope. It receives unfiltered, uncalibrated stray reflected light, and its output is not used in the temperature calculation.

In order to circumvent the problem of two-dimensional flow, a new target fixture has been designed which makes use of a very small sample-thickness to diameter ratio (Fig. 2). This

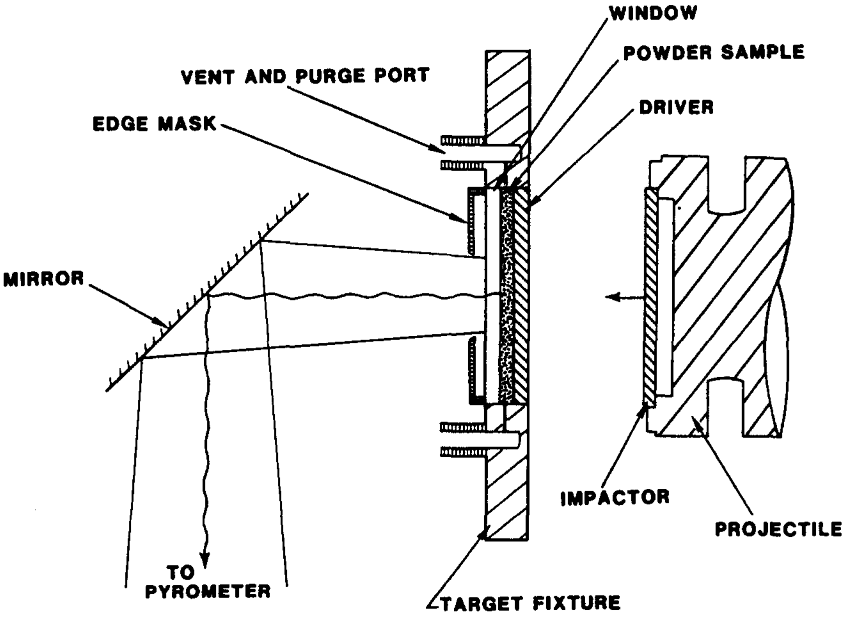

Fig. 2. Detail of target fixture used with powder samples.

fixture also has ports through which purging gas can be flowed and/or air can be evacuated. An upper bound on the amount of light emitted from the sapphire window was obtained by carrying out an experiment on alumina powder. Shock experiments were carried out on pure nickel powder in order to measure temperature increases due to sources other than chemical reactions between Ni and Al powders.

Three experiments on three different powders will be presented here. The powders consisted of: 1) a mechanical mixture of nickel and aluminum, 70% Ni and 30% Al by volume pressed to an initial density of 4.25 g/cm^3. 2) pure nickel at 4.99 g/cm^3 and 3) aluminum oxide at 2.36 g/cm^3. Powders were CERAC N-1095 nickel with particle sizes between 44 and 74 µm, CERAC A-1189 aluminum from 5 to 15 µm, and spherical alumina from 20 to 60 µm. In all three experiments, the impact conditions are the same: gas gun-launched copper flyer plates impact copper drivers at nominal velocities of 1 km/sec. The shock wave passes through the driver and into the powder sample. Peak pressures vary somewhat among the three experiments, as the powders have various shock impedances.

RESULTS

Time-resolved data were obtained at four wavelengths for all three experiments. Data for experiment 2073 (nickel-aluminum) are presented in Fig. 3. The shock wave arrives at the powder-window interface about 2.6 microseconds after the trigger signal. Light that is detected prior to this time is presumably generated within the powder and scattered by multiple reflections through the interconnected pore space ("shine-through"). Release of pressure due to the arrival of the rarefaction wave from the free surface of the window occurs about 0.5 microseconds later. The edge mask aperture insured that the powder was under uniaxial strain during this entire time interval. Air pressure in the target chamber was measured to be less than 2.6 Pa just prior to the experiment. The spectral radiances measured

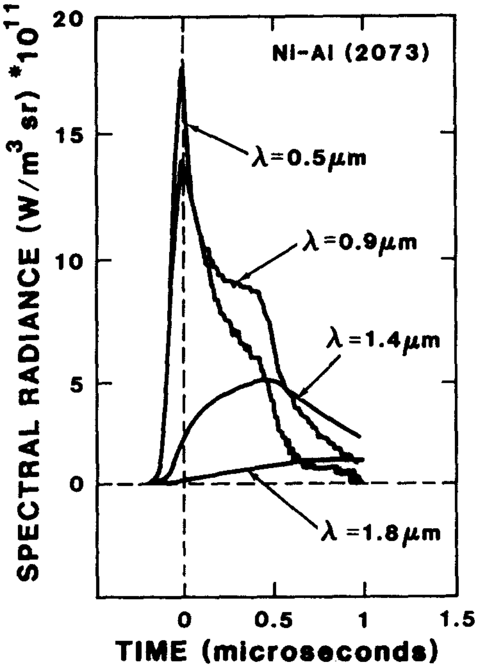

Fig. 3. Time-resolved spectral radiance data from nickel-aluminum experiment 2073 at four wavelengths. Shock wave reaches powder-window interface at time t=0.

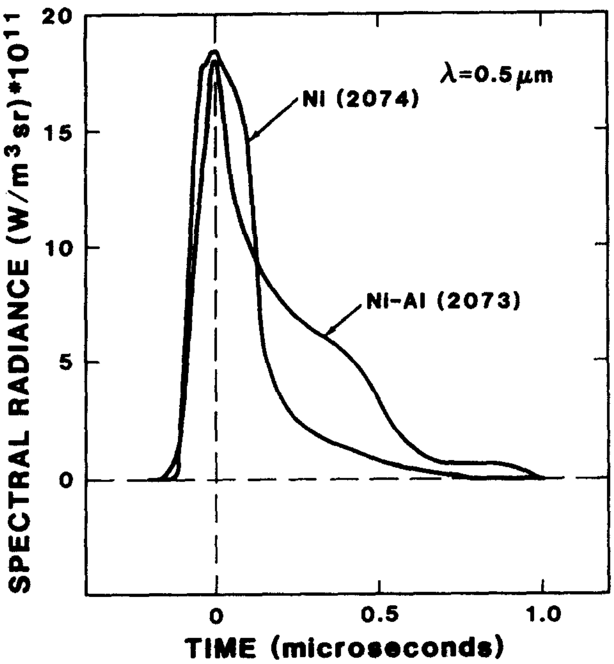

Fig. 4. Time-resolved spectral radiance data at 0.5 µm from nickel aluminum (2073) and nickel (2074) experiments.

in this experiment are similar in magnitude to these measured by Boslough and Graham (1985) in the earlier experiments on this powder mixture. However, single well-defined states are observed in the present experiment due to the uniaxial strain condition. Furthermore, the fact that the sample was in contact with the well-evacuated target chamber demonstrates that the emission of light is not due to air in the system.

Spectral radiances for 0.5 µm light radiated from various shocked powders are compared in Fig. 4. Data from the nickel-aluminum mixture are shown along with data from the shocked end-member nickel (experiment 2074). Peak spectral radiances are almost precisely the same for both nickel and nickel-aluminum at 0.5 µm. This would be expected if the early behavior is dominated by physical, rather than chemical processes, as the mixture is about 87% nickel by mass. Subsequent behavior, however, shows a difference between the powders; the brightness of the mixture decays more rapidly at early times, and more slowly at later times than the brightness of the pure nickel. Time-resolved temperatures determined from the spectral radiances are depicted in Fig. 5.

The experiment on alumina powder was intended to provide a measure of the maximum amount of light radiated from the sapphire window under the loading conditions of these experiments. Experiments on sapphire by Barker and Hollenbach (1970) suggest that its use as an optical window is questionable in this pressure range, while Cremers, Marston and Duvall (1979) measured significant light emission from sapphire. Alumina powder was used in this experiment because it has the same composition as sapphire, and its shock impedence happens to be very similar to that of nickel. Powder was used to simulate the physics of the other experiments, in which the shock arrives at the sapphire window through powder. At 0.5 µm, Fig. 6 shows that the light emission from the alumina experiment is significantly less than that from the

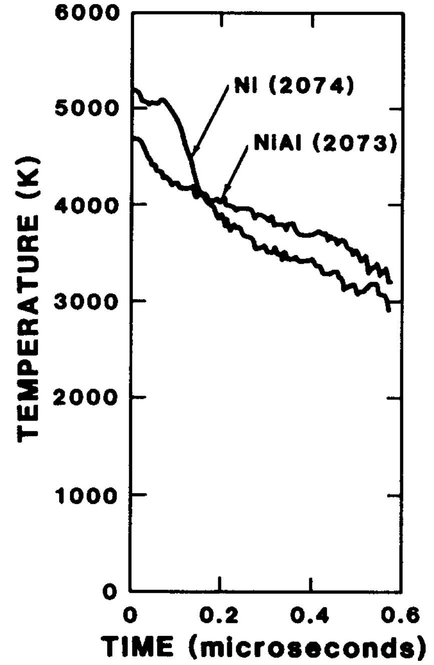

Fig. 5. Time-resolved temperatures for two experiments determined from measured spectral radiances. As implied by increasing "noisiness", error increases with time due to decreasing spectral radiance signals.

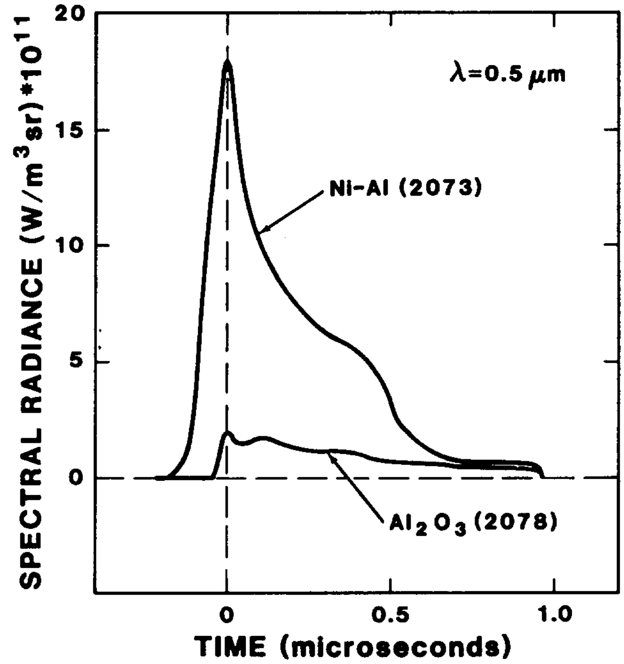

Fig. 6. Spectral radiance at 0.5 µm of alumina powder compared to that of the nickel aluminum mixture.

nickel-aluminum mixture, at least while the powders remain shock-loaded for the first 0.5 µs. At later times, light emission from the alumina appears to become relatively important, because of the drop in brightness of the nickel-aluminum. The measured spectral radiance is, however, an upper bound on that radiated from the sapphire window, as it was impossible from the geometry of the experiment to determine what fractions were radiated from the window, the powder, and the driver-powder interface. It is conceivable that the fraction radiated from the window itself is small.

DISCUSSION

Our understanding of shock-chemistry can be increased from experiments such as these in two ways: 1) something can be learned of the conditions required for chemistry to occur by carrying out real-time experiments, and 2) the reaction itself may be detectable in real time. This will allow models of shock-chemistry processes (e.g. Horie, 1986) to be well grounded in experimental evidence.

Results of the present experiments can be used in the first way, and possibly in the second. The extremely high initial temperature present in the nickel-aluminum mixture surpasses the melting points of both metals, and even their vaporization points at one atmosphere. There is no way of determining the mass fraction of hot material from present experiments. However, it can be crudely estimated by equating the thermal energy gain in a mass at the measured temperature to the Rankine-Hugoniot energy. These energy balance considerations require the mass to be small (about 17%). These small quantities of very hot material can aid the diffusion and mixing rates required for the chemistry to occur on such fast time scales.

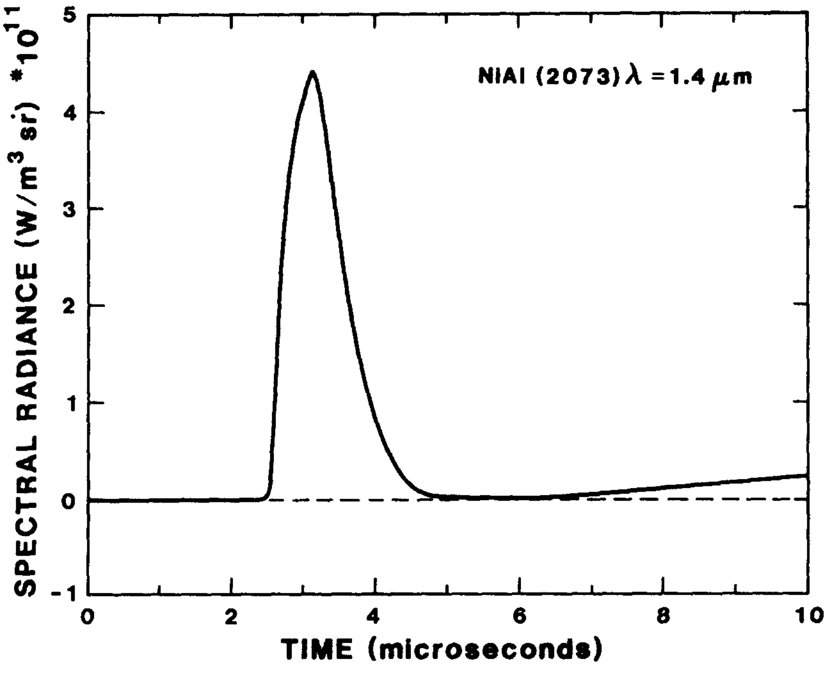

Fig. 7. Data at 1.4 µm for the nickel-aluminum experiment showing a long-term increase in spectral radiance. Absolute time scale is arbitrary.

Use of the present data as a measurement of the reaction in real time is not as straightforward. It is impossible by measuring absolute temperatures of heterogeously heated shocked materials to determine whether or not chemistry has taken place because physical processes such as pore collapse can acheive temperatures high enough to dominate the light emission. However, temperature gains due to exothermic reaction energy can be seen under certain circumstances. First, by comparing the temperature history of a reactive powder to that of an inert powder with the same physical properties, the temperature difference can be explained in terms of chemistry. The nickel-aluminum (reactive) mixture differs from the pure nickel (inert) in the present experiments only by the addition of about 13 weight percent aluminum. The initial shock temperature in the pure nickel is somewhat higher than that of the mixture, possibly because the average void is bigger in the nickel powder (aluminum grains are smaller and tend to fill the nickel voids in the mixture). The initial cooling rate is higher in the mixture. This would be expected, as aluminum has a higher thermal diffusivity than nickel. However, at later times, the temperature of the mixture is higher than that of the pure metal. This is suggestive of exothermic chemistry, but further and more precise experiments need to be undertaken to be certain.

A second way in which exothermic reaction temperatures might be detected is to make observations at longer times. If enough time has elapsed so that the temperature distribution has become uniform, the temperature of a compressed inert material becomes equal to the mean-bulk (continuum) shock temperature. On release, the temperature decreases adiabatically to a residual post-shock temperature. Both of these temperatures can be calculated in a straightforward fashion, and if two materials have the same physical properties, these temperatures should be the same. Again, any differences in temperature can be attributed to chemistry. If the exothermic reaction continues after the temperature distribution becomes homogeneous, the temperature will begin to increase. Fig. 7 shows behavior which suggests this possibility. However, this experiment was not designed for observation times longer the 1 μsec, so the state of the powder, and of the sapphire window at late times are very poorly characterized; flow is two-dimensional, fracture of the window may be taking place, and so forth. A possible method of overcoming these late-time problems would be to use much finer-grained powders. Because of smaller and more numerous pores, initial hot-spot temperatures would be lower, and would equilibrate much faster to a uniform distribution. By the same token the powders would probably react more quickly as the components would not have as far to diffuse. By using powders with sufficiently small grain sizes, the observations of interest could all be made before two dimensional effects take over.

CONCLUSIONS

Observations of light emitted from shocked metal powders demonstrate that extremely high temperatures exist for brief periods of time. It may be these high temperatures which trigger shock-induced chemical reactions in reactive powders, by providing a mechanism for mass diffusion. Subsequent temperature histories show some evidence for heating due to chemical reaction on a submicrosecond timescale. Further experiments will be carried out in an attempt to isolate and quantify this shock-induced reaction in real time.

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REFERENCES

Barker, L. M., and R. E. Hollenbach (1970). Shock-wave studies of PMMA, fused silica, and sapphire. J. Appl. Phys., 41, 4208-4226.
Boslough, M. B., and T. J. Ahrens (1986). A sensitive time-resolved radiation pyrometer for shock-temperature measurements. J. Phys. E., submitted.
Boslough, M. B., and R. A. Graham (1985). Submicrosecond shock-induced chemical reactions in solids: first real-time observations. Chem. Phys. Letters, 121, 446-452.
Boslough, M. B., R. A. Graham, and D. M. Webb (1986). Optical measurements of shock-induced chemical reactions in mixed aluminum-nickel powder. In Y. M. Gupta (Ed.), Shock Waves in Condensed Matter - 1985. Plenum Press, NY. pp 767-772.
Cremers, D. A., P. L. Marston, and G. E. Duvall (1980). Sources of light emission during shock experiments. High Temperatures-High Pressures, 12, 109-112.
Graham, R. A., and D. M. Webb (1984). Fixtures for controlled explosive loading and preservation of powder samples. In J. R. Asay, R. A. Graham, and G. K. Straub (Eds.), Shock Waves in Condensed Matter - 1983. North Holland Press, New York. pp 211-214.
Graham, R. A., and D. M. Webb. (1986). Shock-induced temperature distributions in powder compact recovery fixtures. In Y. M. Gupta (Ed.), Shock Waves in Condensed Matter - 1985. Plenum Press, NY. pp 831-836.
Horie, Y., (1986). Personal communication.

Horie, Y., R. A. Graham, and I. K. Simonsen (1985). Synthesis of nickel aluminides under high-pressure shock loading. Mat. Letters, 3, 354-359.

Horie, Y., D.E.P. Hoy, I. K. Simonsen, R. A. Graham, and B. Morosin (1986). Shock-wave synthesis of titanium aluminides. In Y. M. Gupta (Ed.), Shock Waves in Condensed Matter - 1985, Plenum Press, NY, 761-766.

Lyzenga, G. A., T. J. Ahrens, and A. C. Mitchell (1983). Shock temperatures of SiO_2 and their geographical implications. J. Geo. Phys. Res., 88, 2431-2444.

Pak, H. R., Y. Horie, and R. A. Graham (1986). Synthesis of nickel-aluminum alloys by shock compression of composite particles. In Y. M. Gupta (Ed.), Shock Waves in Condensed Matter - 1985, Plenum Press, NY, 749-754.