CHEMICAL SYNTHESIS UNDER HIGH PRESSURE SHOCK LOADING[+]

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ABSTRACT

Many reports of chemical synthesis under high pressure shock loading have been published over the past thirty years, but little progress has been made in developing an understanding of the mechanisms responsible for the observed effects. Indeed, there remains significant skepticism as to the credibility of many experiments. Certain of the skepticism is based on a "benign shock compression" paradigm in which chemical changes are not expected to occur in a perfect lattice description of solids in thermodynamic equilibrium on the microsecond duration of the shock-compression event. This paper discusses the current status of studies in shock-induced solid state chemistry. It is observed that it is relatively easy to initiate and control chemical reactions in shock-loaded powder materials. In solids it is well known that chemical changes are controlled by defects at all levels from atomic and microstructural to continuum. A major program to study shock-induced modification of inorganic powders provides explicit evidence for unusually large plastic deformation and resulting defect structures. Shock-modified powders also show major enhancements in solid state reactivity in post-shock experiments. Currently, two systems are found to provide a basis for studying controlled chemical synthesis. Intermetallic alloys have been found to be produced in a controlled manner from mechanical mixtures of aluminum with either nickel or titanium. Optical measurements show that a strong chemical reaction is induced on a 100 nanosecond time scale in such aluminum-nickel mixtures under shock compression. The nonferrous metal oxide-ferric oxide system is another promising chemical system in which mixtures of zinc oxide and ferric oxide readily form a zinc-deficient zinc ferrite. Shock-induced chemical synthesis appears to provide a significant opportunity for the synthesis of new materials. Study of chemical effects associated with shock loading provides a new probe of shock-compression processes and current descriptions of the conditions under which they can occur suggest that chemical effects may be ubiquitous in fully dense materials encountered in shock compression studies.

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INTRODUCTION

Shock-induced solid state chemistry has recently become a very active area of research. Observation of chemical changes in shocked solids raised particularly profound questions concerning the state of shock-compressed matter. The mobility of ions in the solid state is so restricted that processes in thermodynamic equilibrium in a perfect lattice will not permit significant changes in chemical state. Based on this perfect lattice paradigm, "benign shock compression," it has proven easy to dismiss observations of reactions in solids as due to uncontrolled post-shock effects of unknown but extreme shock states. It has also proven easy to dismiss experimental observations because the vast majority of the observations are under such uncontrolled, unknown conditions that they cannot bear the weight of critical scientific examination. However, since the inception of modern solid state chemistry in the early twentieth century, the central role of defects for solid state reactions has been recognized [1,2]. Accordingly, a description of shock-compressed matter in a "catastrophic shock compression" paradigm which incorporates the influences of defects at all levels of description, is fundamental for a description of shock-induced solid state chemistry. The most casual examination of the literature in solid state reactivity, solid state chemistry or mechanochemistry and consideration of shock-compressed matter in the defect state reveals that the question is not whether solid state chemistry can occur under shock compression, but how much can occur. The question is not qualitative but quantitative. To what extent are chemical effects operative in particular materials under particular shock-compression circumstances? Are yields and thermodynamic consequences significant?

The question of the behavior of low density powder compacts as a higher temperature analog of processes in solid density materials is also a fundamental issue. Much of the chemical synthesis has been carried out in powder compacts and it is well known that significantly higher mean bulk temperatures are encountered than in fully dense solids. Is chemical reaction a direct consequence of higher temperature consistent with a benign shock view, or are there defect processes inherent in powders not encountered in solids that lead to greatly enhanced solid state reactivity?

These issues were recently considered in the Duvall committee on Shock Compression Chemistry in Materials Synthesis and Processing sponsored by the National Materials Advisory Board of the National Research Council of the National Academy of Sciences [3]. A key finding of the report was "as a result of its deliberations, the committee finds that there are substantial grounds for believing that novel physical and chemical processes are involved in the compression and heating of materials by shock waves and that some of these processes may ultimately serve as the basis for useful technologies."

In the present paper an overall assessment of recent work on shock-induced solid state chemistry in metallic and inorganic substances is presented.

BACKGROUND

The shock-induced solid state chemistry program in which the present authors are involved was initiated in about 1980 after a recognition that chemistry in shocked solids, like electronic effects, is controlled to a large degree by defect-centered rather than perfect-lattice centered models. A major program in the Soviet Union, as summarized by Gol'danskii and coworkers [4,5], raised intriguing questions about the shock process but has provided few answers. After our first experiments it became apparent that it was very easy to cause chemical changes under shock compression. It was clear, however, that complex and unique processes were involved and that a long range, systematic, quantitative study was required. Two factors were thought to be critical: 1) methods for quantitative, reproducible shock-modification and preservation of samples for post-shock analysis over a wide range of shock conditions and, 2) study of shock-induced defects and microstructural features and their relationship to shock-enhanced solid state reactivity.

Recovery Fixtures

The study of samples which have been subjected to controlled shock loading and preserved for post-shock analysis provides the major foundation upon which shock-induced chemistry rests. Although other probes, particularly optical methods, afford an opportunity to directly probe the shock-compressed state, the limited information content is not sufficient to define a chemical process in most solids. The shock-recovery experiment provides quite explicit and detailed information but the sample is produced as the result of a complex process of loading and unloading. As a result, although the material held in the hand is the essence of all materials science, it is not easy to identify particular material features with particular features of the shock process. Nevertheless, the recovered samples contain vital information not available from other sources and many studies of materials-centered processes (for example rapid quenching) suffer similar limitations. The recovery experiments mimic in many ways the early days of chemistry in which substances were mixed and the resulting reaction products studied. In the hands of skilled scientists of different disciplines, a great deal can be learned and what is learned will not come from other experiments.

Careful study of shock compression conditions in sample recovery fixtures has shown that quantitative specification requires two-dimensional numerical simulation [6-9]. Much of the earlier work on chemical synthesis has been carried out under conditions which cannot be independently confirmed and it is now apparent that statements about pressure and temperature achieved based on one-dimensional analyses are substantially in error. The fixtures used to acquire the data reported by our group provide all the features needed for quantitative, reproducible scientific studies. It should be recognized, however, that the loading conditions are considerably more complex than that encountered in uniaxial strain in a solid density sample. Although shock conditions are stated with significantly greater errors than in wave profile measurements, they are sufficiently accurate to draw stated conclusions and are subject to refinement if required.

Enhanced Reactivity

It is possible to develop quantitative descriptions of the extent that shock modification increases the solid state reactivity by studies in the post-shock condition. Examples studied include: solid-solid reactions, solid-liquid reactions, solid-gas reactions, structural transformations and powder-consolidation processes. In Fig. 1, examples of four of the processes are shown. Figure 1a shows differential thermal analysis (DTA) traces recording the reaction of mixed powders of zirconia and lead oxide [10]. The upper trace is for unmodified zirconia, the middle trace is for a sample shock-modified at a peak pressure of about

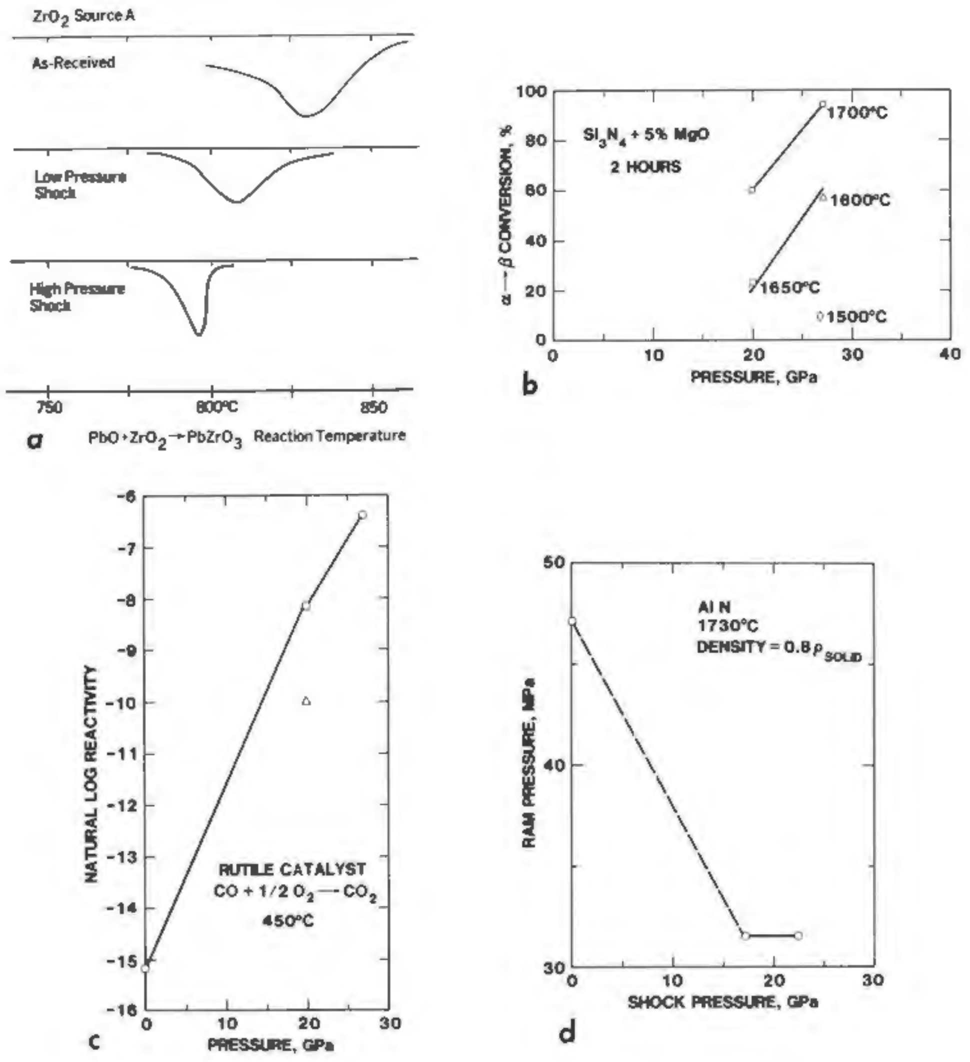

Figure 1. Examples of shock-enhanced solid state reactivity of powders preserved for post-shock study are shown. a) is a differential thermal analysis trace of the reaction of lead oxide and zirconia. (Exothermic temperature is downward.) b) shows the structural conversion of silicon nitride upon heating observed for modification at different shock pressures. The conversion is due a dissolution-precipitation process. c) shows the catalytic activity of a shock-modified rutile catalyst in a flow reactor used for the oxidation of carbon monoxide. d) shows the ram pressure required to achieve a density of 80% of solid density in a hot pressing experiment on aluminun nitride.

22 GPa and the bottom trace is for a powder modified at a pressure of about 27 GPa. The DTA trace for the most strongly modified zirconia has a similar appearance to that of a zirconia sample with a very large specific surface. These measurements show a strongly shock pressure dependent increase in solid state reactivity such that the shocked zirconia, with a modest specific surface, reacts much like a more conventional powder with a large specific surface.

In Figure 1b, the conversion of shock-modified α-phase silicon nitride to a β-phase upon heating is shown [12]. This conversion can only result from a dissolution-precipitation process and the shock modification can only affect the dissolution. The experiments indicate a greatly enhanced dissolution rate for the shock-modified powder. The extent of the effect is a strong function of the shock-modification conditions.

In Figure 1c, the catalytic activity of shock-modified rutile is compared to standard material for the oxidation of carbon monoxide in a flow reactor [11]. The enhanced catalytic activity is found to be substantial and controlled by the shock conditions. The enhanced catalytic activity is a result of shock-induced defects which greatly affect surface states.

Finally, in Figure 1d the consolidation rate under hot pressing is shown for shock-modified aluminum nitride at 17 and 22 GPa shock pressure [13]. The consolidation rate is found to be substantially higher in the shocked material. Control experiments have demonstrated that a recrystallization process of the highly defective shock-modified powder under the stress of hot pressing is responsible for the higher rates of consolidation. The resulting microstructure of the hot-pressed, shock-modified aluminum nitride is unique [13].

The four explicit, quantitative examples of greatly enhanced solid state reactivity serve to demonstrate that shock-induced defects and microstructural features are readily introduced by shock loading and that they can have a dramatic effect on chemical changes in the solid state. In none of the examples, or others which have been studied, are there changes in particle specific surface large enough to affect reactivity.

Shock Modification

Our early synthesis work led us to believe that modeling of shock-induced chemistry required substantially improved understanding of shock modification of inorganic materials. Accordingly, a significant effort in shock modification of inorganic powders involving numerous materials has been carried out. Table 1 lists materials which have been studied to a significant degree. Other materials have been studied less extensively or are currently being studied. A range of material probes has been employed to characterize the shock-modified samples. Studies of particle morphology have been carried out with scanning electron microscopy (SEM), particle distributions from computer processing of SEM photographs (Quantimet), specific surface measurements and optical microscopy. Atomic level defects and microstructural features were studied with x-ray diffraction line broadening, electron spin resonance (ESR) and transmission electron microscopy (TEM). For magnetic materials, static and dynamic magnetization and Mössbauer measurements were carried out. Differential thermal analysis of energy release on heating and cooling was employed in a number of cases and consolidation behavior upon sintering was sometimes studied. Although observations with the unaided human eye are not quantitative, it proved obvious from visual inspection of many materials that very substantial changes are induced by shock compression. All materials were not studied with all probes, but typical analysis included a number of the different material characterizations. The present shock-modification effort is probably the most extensive ever undertaken. In most cases, shock conditions of pressure and temperature were varied over a wide range in a quantitative, reproducible manner.

Table 1. Shock-Modified Materials Studied

Minerals
- Pyrite

Oxides
- TiO_2 rutile
- TiO_2 anatase
- ZrO_2
- Al_2O_3

Nitrides
- AlN
- Si_3N_4

Carbides
- TiC

Borides
- TiB_2

Antiferromagnets
- Fe_2O_3

Ferrites
- Fe_3O_4
- $CuFe_2O_4$
- $NiFe_2O_4$
- $CoFe_2O_4$

Crystals
- Quartz
- Lithium niobate
- Rutile

Mixed Powders
- $PbO + ZrO_2$
- $ZnO + Fe_2O_3$
- 30 % Al-Ti
- 30 % Al-Ni
- 6 Al-Mn

Complete results of the shock modification program are too extensive for inclusion in the present paper and many have been published [14-20]. Several overall features are of particular note. It is well known that greatly enhanced solid state reactivity can be achieved by particle size reduction and increase in specific surface. Careful, consistent specific surface measurement show that shock-modified materials exhibit only modest changes in specific surface. It can be confidently stated that shock-enhanced solid state reactivity is not the result of increases in specific surface.

X-ray diffraction provides one of the most direct and universally available tools for the study of residual strain and crystallite size reduction caused by shock compression. The method also provides a direct indication of structural or chemical composition changes. Morosin and coworkers have carried out numerous detailed analyses of a large number of shock-modified materials [14,20-24]. The studies show that care must be given to the analysis as shock-modified materials differ from those derived from other processes. The overall material response is illustrated in Figure 2. Although most of these materials are brittle and rarely undergo plastic deformation in conventional environments, it is observed that plastic deformation is readily produced under shock loading. The shock pressure required to initiate residual strain is low, of the order of 1 GPa or less. Only in the case of titanium carbide and titanium diboride is a significant critical pressure required to initiate deformation.

The material-dependent and pressure-dependent behavior that is most prominent is the pressure to achieve a saturation level of residual

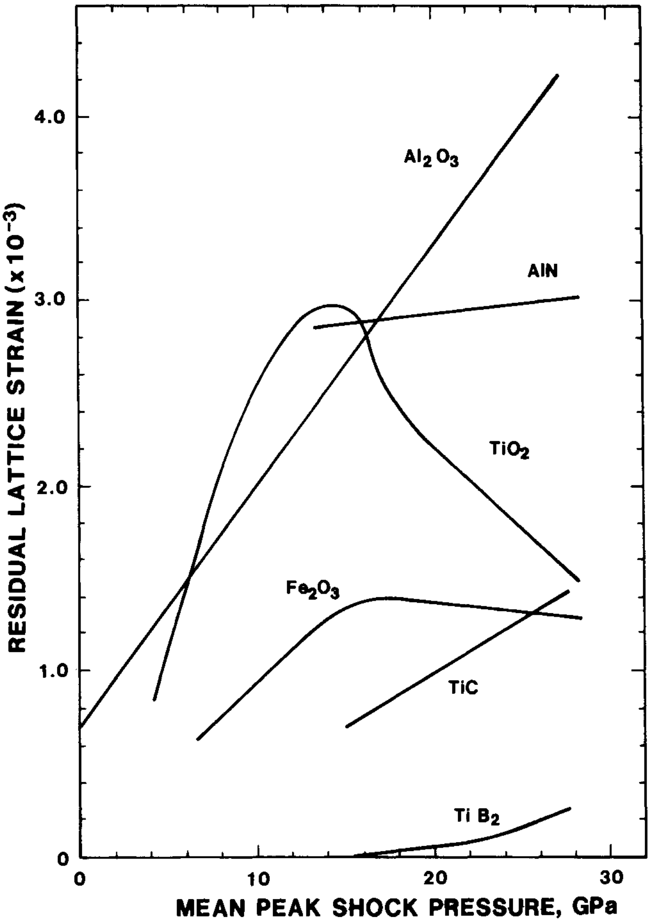

Figure 2. Residual strain observed in shock-modified inorganic powders shows that they are readily deformed plastically under shock compression. Only titanium carbide and titanium dibodride show a significant pressure to initiate plastic strain.

strain. This saturation strain value is about 5 x 10^{-3}, a value characteristic of heavily worked metals. TEM observations confirm the extensive plastic deformation and typically show such a high defect density that individual features of dislocations cannot be resolved. At higher pressures, rutile is observed to show less residual strain than at lower pressures. This behavior is thought to be the result of post-shock annealing.

The plastic deformation observed in these brittle refractory materials is extraordinary and is a shock-modification feature not found in other processes.

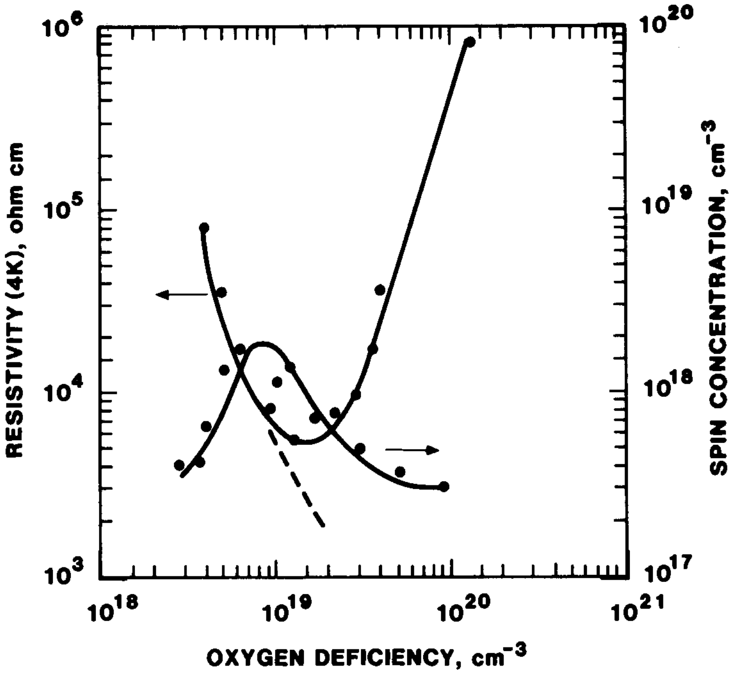

Figure 3. Prior work by Hasiguti [27] in relating oxygen deficiency to resistivity and paramagnetic spin concentration shows a critical behavior at a deficiency of about 10^{19}. Shock-modified rutile achieves larger spin concentrations (about 10^{19}) and lower resistivities (about 10^{-4} ohm-cm) at microwave frequencies.

Shock-induced point defect concentrations provide a particularly sensitive probe of defect processes. It has long been recognized that shocked metals contain unusually large concentration of vacancies due to the high speed motion of dislocations [25]. Venturini and coworkers (15,26) have carried out an unusually broad and thorough study of shock-induced paramagnetic defects with electron spin resonance (ESR). In general what is seen is very large defect concentrations indicative of large plastic deformation and defect states produced in a highly nonequilibrium manner. Defect concentrations are highly dependent on the particular material and on the particular pressures and temperatures achieved. In rutile, reductions in defect concentrations at higher shock temperatures indicate that there is a significant post-shock annealing in some cases and that during the shock process concentrations are significantly higher.

In the case of rutile, where there is substantial prior work [27] on defects induced by other processes, the unusual nature of shock defects is readily apparent. Based on prior work, it is known that as oxygen vacancies are introduced that low temperature resistivity is reduced and paramagnetic defect concentrations of Ti^{3+} interstitials are increased. However, as shown in Figure 3, at a critical oxygen deficiency the behaviors reverse. The minimum in resistivity and the maximum in paramagnetic spin concentration is unlike that observed in other narrow gap semiconductors such as germanium and silicon. Prior studies have indicated that the critical behavior is due to the formation of higher-order point defect complexes which eventually lead to a "crystallographic shear" configuration involving a planar array of oxygen vacancies.

Shock-modified rutile shows a substantially different behavior. Paramagnetic spin concentrations of Ti^{3+} interstitials are $10^{19}cm^{-3}$, far in excess of those achieved in prior work. This higher concentration defect state leads to a metallic-like conductivity at microwave frequencies. TEM studies show no evidence for crystallographic shear. It is apparent from ESR and TEM studies of rutile that the intense, rapid nature of shock deformation has led to a defect state not previously achieved.

As a final example of the role of shock deformation in inducing defects, studies on α-hematite are particularly revealing. Well characterized powders were shock modified over a wide range of shock pressures and temperatures and subjected to detailed static and dynamic magnetization study. Magnetization measurements provide a particularly sensitive probe of shock-induced defects as α-hematite is an antiferromagnet with zero net magnetization in the perfect lattice. The antiferromagnetism arises from iron magnetic moments which are ferromagnetically coupled within a (111) sheet and directed perpendicular to this sheet. In successive atomic layers the moments are antiparallel. Because of this arrangement, any disorder affecting parallel and antiparallel domains can have a major effect on magnetization. The nature of the disorder on the atomic scale cannot necessarily be determined from net magnetization, but Mossbauer effect measurements are in progress which reveal interesting and unusual features [28].

Magnetization observed for shock-modified hematite as a function of peak shock temperature (which involves shock pressure) is shown in Figure 4. The effect of shock modification is seen to be very large; a

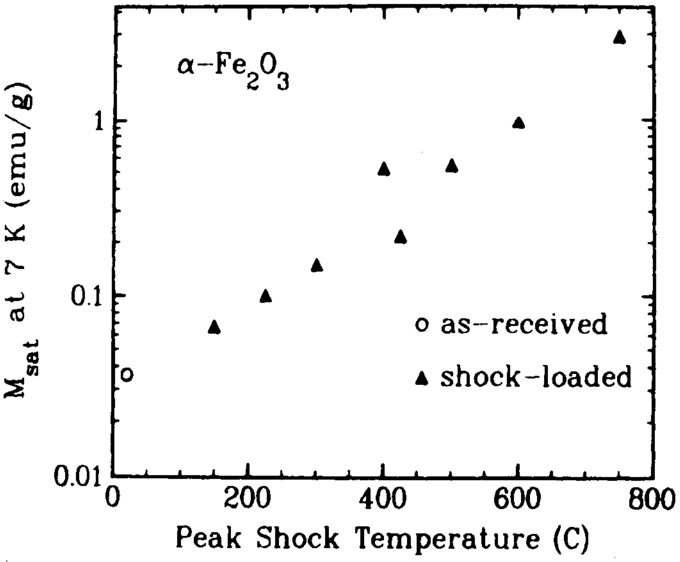

Figure 4. The low temperature magnetization of hematite is strongly altered by shock temperatures (and pressures). At the two highest temperatures, the measurements indicate that a 1% and 3% conversion to magnetite is responsible for the magnetizations shown.

two order of magnitude increase in magnetization is observed. Shock deformation has proven to be extraordinarily effective in introducing defects in hematite. At the two highest temperature points the magnetization results from formation of about 1% and 3% magnetite.

SHOCK-INDUCED CHEMICAL SYNTHESIS

The shock-induced modification studies leave us with explicit physical and chemical characteristics of materials from which we can infer whether conditions in various parts of the shock process can lead to chemical reaction. If chemical reactions are to occur on the submicrosecond or microsecond duration of the shock process when the material is at pressure and accelerating to high speed, the shock-compression must induce a state of greatly enhanced solid state reactivity. In the pressure release phase, events may occur which are not possible at pressure and the rapid decrease in material velocity provides accelerations whose overall directions are opposite but less severe than those in the loading process. Finally, if the sample is well contained in a fixture in the immediate post-shock state, the material will cool through thermal conduction and may be at a modest residual pressure in the fixture.

The shock-modification study shows that, in most cases, significant increases in reactivity due to increases in particle specific surface area are not to be expected. On the other hand, it appears quite likely that enhanced solid state reactivity induced by defects will be maximized. This optimization of defect reactivity is not encountered in other processes and is a unique feature of the shock process. Unfortunately, because this defect state cannot be fully achieved otherwise, a limit to the enhanced reactivity cannot be assessed from other independent studies at present. Greatly enhanced diffusion and significantly increased ease in nucleation will result from the highly defective state. Local stress and temperature gradients can be extreme and lead to enhanced diffusion as will chemical concentration gradients. The very large particle deformation and increase in defect density would be expected to produce surface conditions in which oxides and other impurities have been removed. Such atomically clean surfaces are known to be highly reactive. The overall effect of the shock modification would be expected to achieve very large enhancements in solid state reactivity, but the relative contribution of different aspects of the modification and quantitative specification of the processes must await further experimentation and analysis.

Two systems have been chosen for detailed chemical synthesis study: a nonferrous metal oxide (zinc oxide) plus ferric oxide (hematite) and intermetallic reactions between aluminum and nickel and aluminum plus titanium. The specific materials chosen have interesting properties in themselves and represent systems in which many other candidate reactions can be studied. Both synthesis systems have been carefully studied under other conditions. Both systems give large yields of reaction products under shock loading which can be readily controlled by varying the shock conditions. Both systems lend themselves to straightforward but revealing analysis of the reaction products. The intermetallic reactions are strongly exothermic while the ferrite reaction involves essentially no significant energy release.

Zinc Ferrite Synthesis

Ferrites as a class have been extensively studied and the relationships between magnetic properties and atomic level configurations are well understood [29]. Stoichiometric zinc ferrite is not usually used in device applications but it is studied in conjunction with other compositions. Because the stoichiometric composition is paramagnetic and the starting zinc oxide is nonmagnetic, the synthesis products can be explicitly studied with magnetization. Prior work [30,31] has shown a zinc ferrite could be synthesized under unknown shock conditions from starting mixed powders of zinc oxide and hematite. Typical conventional synthesis is carried out as a solid state reaction between mixed powders heated in a controlled oxygen environment. It is known that the formation of oxygen vacancies in hematite is critical to the promotion of diffusion of zinc into the hematite.

Four material probes were used to study the shock-synthesized products. Of these, magnetization provided the most sensitive measurements, X-ray diffraction the most explicit structural data, Mossbauer the most explicit atomic level data and, although TEM was used on only a limited number of samples, it provides the most explicit chemical composition and microstructural data. All four probes reveal a somewhat different material description. The differences emphasize the need for a wide variety of materials characterization before detailed models of unique materials can be confidently developed.

Mechanically-mixed powders in a stoichiometric ratio to form $ZnFe_2O_4$ were subjected to a wide range of shock conditions of pressure and temperature and detailed by Morosin, et al [32]. In this work, structural properties of the synthesized products and unreacted components are shown based on X-ray diffraction. Magnetization measurements on certain of the samples are reported by Venturini, et al [33], Mossbauer measurements by Williamson, et al [34] and TEM by Carr and Graham [35]. The results of determinations of yield of products by the various techniques are summarized in Figure 5. In the figure, bar graphs are used beside the points in pressure and temperature at which yields were determined by the different techniques. X-ray diffraction yields are based on the relative amount of material in the spinel structure. Yield based on magnetization is based on prior magnetization studies. Mossbauer measurement show two spinel phases, one ferrimagnetic and one paramagnetic. Both products are shown. In this figure only results based on Composition B explosive loading are shown as the yields obtained from baratol explosive were consistently lower. (This observation is thought to provide explicit evidence that the amplitude of the initial low pressure wave has a significant effect on the chemical reaction because the early loading history is strongly affected by the type of explosive.)

From Figure 5 it is notable that magnetization provides the most sensitive detection of reaction products. Even at the lowest pressure and temperature a detectable magnetization occurred. This magnetization is over and above that due to hematite modification. Detectable yield at such modest loading conditions, which is also observed in the intermetallic synthesis, provides explicit evidence for the extraordinary efficiency of mechanically-forced reaction due to shock compression.

As indicated in Figure 5, X-ray diffraction showed that the yield of spinel-structure zinc ferrite was a strong function of shock pressure and temperature. Yields were very large, up to 85% in the most extreme pressure and temperature case. Line broadening due to strain, reduced crystallite size and possible inhomogeneities was significant in all

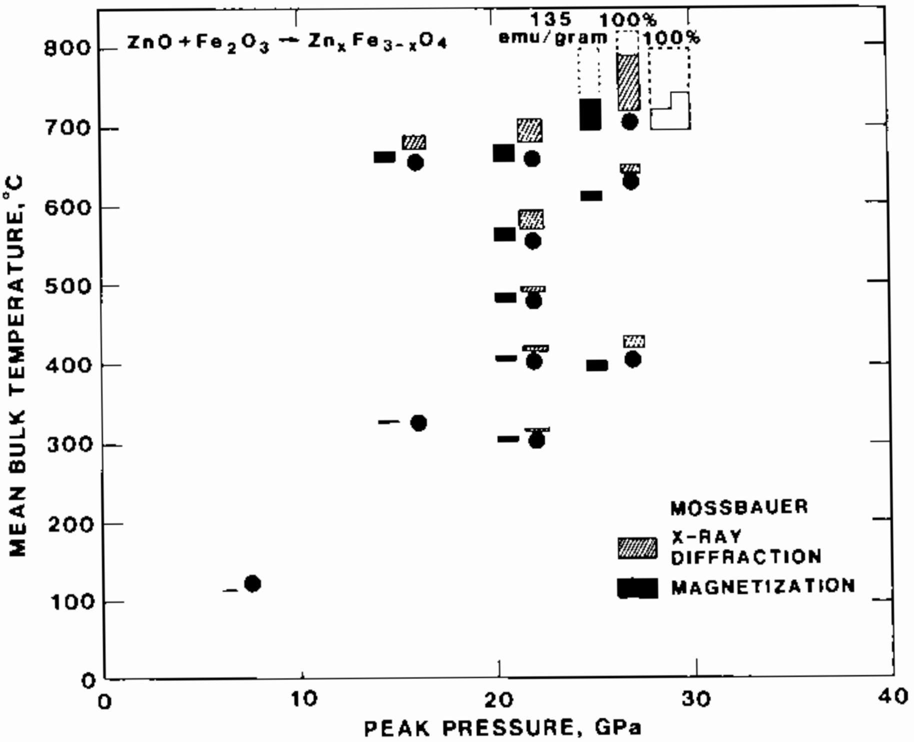

Figure 5. The yield of shock-synthesized zinc ferrite is shown to be strong function of shock pressure and shock temperature. Bar graphs beside the points at which experiments were conducted show the yields determined by the three techniques. Magnetiztion shows detectable yields at the lowest pressure. Mossbauer includes two different spinel-structure components.

samples except at the most extreme shock condition at which a dramatic sharpening of diffraction lines occurred. Although there is a hint of a threshold for reaction of 15 GPa pressure and a temperature of about 300 C, the detection limit is about 5% and, as indicated below, magnetization showed ferrite yield at the most modest shock condition. The yields of spinel are in good agreement with the Mossbauer data. X-ray diffraction indicated that the starting powders were not fully consumed in the reaction. More hematite was consumed relative to zinc oxide, suggesting that the spinel is zinc deficient. The sharp lines observed in the most extreme loaded sample permitted a determination of a zinc compositiom of 0.92.

Mossbauer spectroscopy showed three distinct iron resonances in the shocked material. One of these is due to iron in the shocked but unreacted hematite and its characteristics match those of hematite shocked in independent experiments to the same shock conditions. The Mossbauer data are explicit in demonstrating that changes in magnetic properties are due to the reaction products, not some defect-induced structural modification of hematite.

The second magnetic phase is identified as a zinc-deficient ferrite $Zn_xFe_{3-x}O_4$ with x = 0.2. The data indicate that the composition is independent of shock condition; it is the yield which is strongly affected.

The third phase is paramagnetic in character and present indications are that it is superparamagnetic due to a relaxation phenomenon for domain sizes in the range of about 500 nm.

Based on the combination of data shown in Figure 5, it is apparent that magnetization measurements provide the most sensitive detection of reaction products. Even at the lowest pressure and temperature, a detectable magnetization was observed.

Based on the magnetizations observed, the ferrite is composed of a zinc-deficient ferrite with zinc composition between 0.4 and 0.6. As is observed with Mossbauer, yield is strongly dependent on shock condition but composition remains the same.

The TEM study was more limited in scope than the others and included only the starting powder mixture, a shocked but only modestly reacted sample and the sample subjected to the most extreme conditions. As indicated earlier, the most extreme conditions appear to have produced a ferrite with significantly different characteristics. The starting powder was found to be well blended down to the individual grain level. Grain sizes were about 200 nm. Both powders showed low defect density. No ferrite was found in the modestly shocked sample. Only hematite grains could be easily located; the softer zinc oxide flowed between the harder hematite grains. X-ray energy dispersion spectroscopy scanning (EDS) across "grain boundaries" showed heavy concentrations of zinc between hematite grains. Some hematite grains were found to contain up to 5% zinc.

At the most extreme shock condition ferrite grains about 500 nm in size were readily apparent and were found to be defect free. They appear in clusters up to 10,000 nm across. The appearance of the grains demonstrates they have gone through a recrystallization process. There was no evidence for compositional gradients within the grains. The material between the clusters was observed to be a well mixed conglomerate of the starting materials. As this sample is the only sample showing recrystallization and the yield is much greater than other samples, it is tempting to relate the recrystallization process to higher yields. The composition is found to have a zinc value between 0.89 and 0.93 which agrees with that determined from X-ray diffraction lattice parameters.

The various material probes provide what is, on the surface, a major disagreement concerning the chemical composition of the synthesized ferrite. EDS provides a direct measurement of the composition but the technique has only been used on the sample subjected to the most extreme shock conditions. At this extreme condition both X-ray diffraction and TEM provide zinc concentrations in agreement with each other and close to a stoichiometric composition. Neither of these determinations agree with the magnetization or Mossbauer data which, depending on interpretation, can give zinc values between 0.2 and 0.6. It should be recognized however that concentrations with the latter probes do not provide a direct measure of the concentration. Values are derived indirectly from published reports in which the relationships between magnetization or Mossbauer parameters were established on ferrites synthesized by conventional methods. Resolution of the differences must involve consideration of the possibility that the shock-synthesized material is substantially different from other compositionally similar material.

Intermetallic Synthesis

Intermetallic alloys or compounds are a particularly interesting class of materials which have been widely studied because of important technological applications. The aluminides have been identified as compounds with highly desirable characteristics of high temperature strength and resistance to corrosion. It has proven difficult to prepare suitable aluminides with good properties as impurities at grain boundaries have acted to greatly reduce the ductility. Our group has carried out the first synthesis of nickel and titanium aluminides under shock compression [36] as well as a detailed study of the relationship of reaction products on shock compression conditions. The experiments and analysis are extensive and only an overall summary can be presented. Other papers in this proceedings by Horie and coworkers [37-40] contain more detail.

Although most synthesis in the binary system is carried out from the melt or by rapid quenching or sustained high temperature synthesis, intense mechanical working by cold rolling or high energy ball milling are known to produce amorphous alloys. Thus it is to be expected that intense mechanical deformation of the shock process will have a significant effect on reaction.

Three powder mixtures have been studied. They were a mechanically-blended mixture of aluminum and nickel in an approximate stoichiometric ratio to form Ni_3Al and an equivalent mixture of aluminum and titanium. A less extensively studied composite of spherical particles of aluminum coated with nickel was also examined. For the composite particles the constituents were about 80 weight percent nickel and 20 weight percent aluminum. Starting and shock-modified materials were characterized by x-ray diffraction, TEM, optical microscopy and electron-probe microanalysis.

The mechanically-blended aluminum-nickel powders provided the most definite results. Strong reactions were observed with yields of up to 80 to 90%. Many reaction products were observed and their strong dependence on shock conditions allow identification of local reactions as precursors to the principal reaction product. At the higher shock pressures and temperatures a characteristic pattern of reaction products were observed. In the outer region of the sample, where numerical simulation shows a higher temperature, a large area of almost fully reacted Ni_3Al is observed. In the center part of the same sample where the temperature is lower and the pressure is higher, local reaction regions of NiAl are observed. In a thin transition region next to the Ni_3Al there is a thin region of Ni_2Al_3 which surrounds a eutectic system of $NiAl_3$ and Al. No amorphous materials are detected although there are numerous regions of extremely well mixed substituents in unreacted regions.

As indicated in Figure 6, the yield of reaction products is strongly dependent on shock pressure and temperature. The NiAl product is formed at very modest pressures and temperatures. As in the case of the zinc ferrite synthesis, this observation is thought to be clear evidence for initiation of reaction due to mechanical action. As pressures and temperatures are increased past a critical value of about 500 C and 15 GPa, the Ni_3Al product is observed over an area encompassing the entire region which was above the critical temperature. Due to the large extent of this area and the strongly exothermic nature of the reaction, temperatures of thousands of degrees are expected and the final product would have resulted by pressure quenching and cooling by thermal conduction from the melt. There is evidence from the sample shocked to the highest pressure state that excess pressure (above about 20 GPa) inhibits the initiation of strong reaction.

All reaction products identified have been seen in prior synthesis; what is different is the absence of amorphous material and the presence of Al_3Ni and Al_3Ni_2 which has not been seen in the extensive work on fast quenching of ion-implanted layers with pulsed-electron-beam heating [39]. The shock-synthesized Ni_3Al appears to have microstructural features not

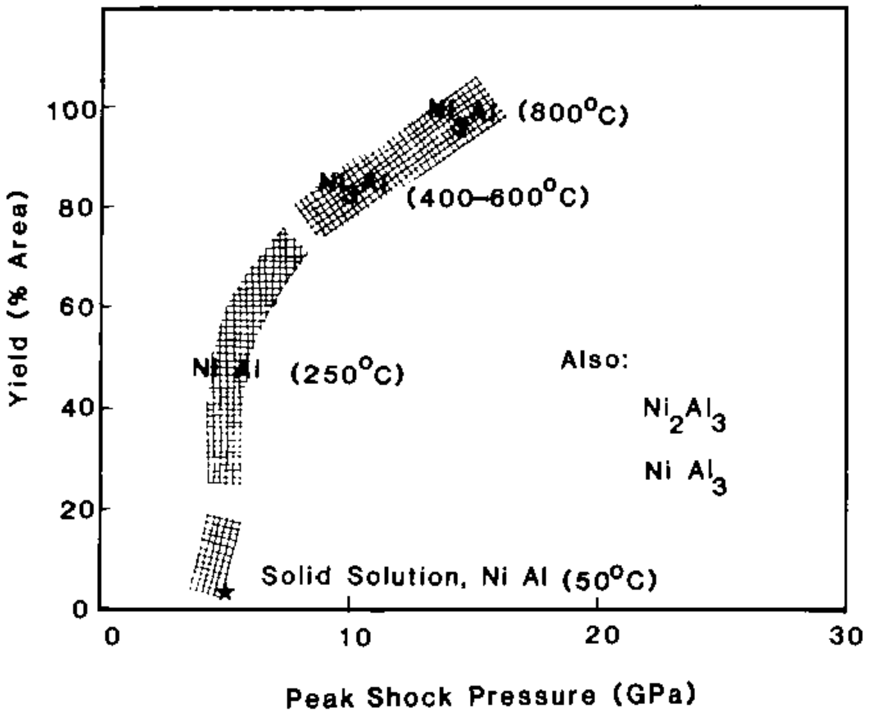

Figure 6. The yield of the indicated reaction products is found to be significantly dependent on shock pressure and temperature. Specific locations of yield determinations are shown with the compound designated. Regions between are shaded by inference. Not shown is the reduction of yield at pressures above 20 GPa.

previously observed. The microhardness is in the range of a heavily cold worked composition even though TEM observations show few dislocations. The hardness is apparently due to an unusually small crystallite size (about 2 nm.) Such material would be expected to have ideal properties for a wide variety of applications.

The smooth sequence of shock-modified features and reaction products leads to a description of the reactions in which early in the shock process the individual grains are heavily deformed leading to a highly defective state and clean surfaces. There is then an extremely efficient mixing process which involves fluid-like flow of aluminum around and into open areas of nickel. Nickel is also mixed into aluminum rich areas. The nickel-aluminum reaction appears locally but is not sustained over large areas. These locally-reacted regions can then serve as nucleation sources when sufficiently high temperatures and larger mixing intensity are achieved. The products in the transition region next to the strongly reacted regions likely result from the high temperature achieved due to a strong exothermic energy release.

In the composite powder, there appears to be a different initiation threshold for strong reactions. A major change in particle morphology is seen resulting from flattening of the composite particles at relatively low pressures. Local regions of Ni-Al are found within nickel-aluminum grains at their interfaces and 100 nm size regions of Ni_3Al are found inside the NiAl.

The titanium-aluminum powder mixtures react far less strongly. Yields are limited and products more difficult to identify. As in the Ni-Al system, the largest region of reaction was found in the outer part of the sample where the temperature is higher than in the center. The product in this region is hard to identify but apparently corresponds to $TiAl_3$ which is difficult to distinguish from the ordered superstructures Ti_9Al_{23} and Ti_8Al_{24}.

The chemical synthesis of intermetallic alloys or compounds from mixed powders of aluminum-nickel and aluminum-titanium has provided an extraordinary rich storehouse of reaction products and shock-activated but unreacted products on which to build models of shock-induced solid state chemistry. There is no evidence that shock-induced melting of the aluminum is necessary to initiate the reaction.

OPTICAL OBSERVATIONS

Recent observations of Boslough and coworkers [41,42] appear to provide the most significant result achieved to date in shock-induced solid state chemistry. The study used optical pyrometry and high speed optical streak observations and provided explicit time-resolved and spacially-resolved data on temperatures associated with shock-induced reaction between aluminum and nickel powder mixtures described above. The observations are particularly significant in that they clearly demonstrate that chemical reaction in shock-compressed solids can be initiated within about 100 nsec after critical shock conditions are achieved. The observations also tie together the numerical simulation of shock processes in recovery fixtures and the recovery experiments which show strong reaction initiating in the same part of the sample in which large yields of intermetallic compounds were observed. Once it is recognized that solid state chemical reactions are possible on such a short time scale, consideration of shock conditions in solid density materials establishes that chemical reactions are likely to be ubiquitous in a wide range of conventional materials. Optical measurements promise to provide explicit data on heat of reaction in shock-induced chemical reactions in solids.

SUMMARY

Although considerable progress has been made in identifying the processes important to shock-induced solid state chemistry, it is clear that there are few quantitative data on which to assess their relative importance. The work summarized in the present paper provides a major source of material response data on shock activation, shock modification and shock synthesis.

The available data indicate that shock-induced solid state chemistry must be based on a catastrophic shock description involving the defect state, nonequilibrium thermodynamics and changes in material configuration occurring at high speed. Chemical reaction under shock compression involves generation of large numbers of defects which can act to greatly enhance solid state reactivity. Plastic deformation of particles has a major effect on configuration and morphology which will lead to a surface cleaning essential for significant solid reaction. The intense material velocities will lead to very efficient mixing. It is clear that there are processes encountered in low density powder compacts that do not occur at solid density.

Optical observations of chemical reactions in powders compressed to solid density while under shock compression remove a conceptual barrier that has prevented serious consideration of chemical reaction in solids on the submicrosecond time scale. With the recognition of the possibility of fast reaction in shock-compressed solids, it is well to inquire as to whether similar effects are possible in solid density samples. What is required for reaction is the presence of different chemical species, a localized increase in temperature and a material mixing. Different chemical species are present in most materials as precipitates or impurities concentrated at grain boundaries. Localized deformation at grain boundaries, at precipitate interfaces and in deformation bands in the bulk will lead to high local temperatures on a transient time scale. The high speed motion of defects and localized deformation at different velocities can then lead to sufficient mixing to initiate chemical reaction and cause it to grow to critical size [40]. Indeed it appears that evidence for such shock-induced solid density chemistry is already published but previously unidentified.

Hill and Rack [43] have reported a TEM study of a Nitronic stainless steel in which an unidentified phase was observed at the intersections of deformation bands. This phase appears to be a sigma phase characteristic of chemical reaction which normally requires hours at elevated temperature but the rate of reaction is known to be greatly accelerated by cold working.

In his interesting historical account of the development of shock compression science at Los Alamos [44], John Taylor closes the article relating a conversation with John Walsh concerning elastic-plastic behavior in which it was agreed "We're in the metallurgical mud." It appears now that we are also in the chemical ooze. If we are to extract ourselves from this ooze perhaps we need to recognize the situation "of the hypnotic power of mental habitudes" posed by the eminent Swedish solid state chemist J. Arvid Hedvall when he related the resistance he encountered in developing solid state chemistry in the early twentieth century [45].

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