ISSUES IN SHOCK-INDUCED SOLID STATE CHEMISTRY

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ABSTRACT

There has been considerable work over the past few years to study shock-induced solid state chemistry. In the present report, issues raised in the area are reviewed and critical concepts are discussed. The distinctive nature of solid state chemistry compared to liquid and gas phase chemistry is emphasized and material probes suitable for the study of solids are described. In order for solids to react in times less than one microsecond, unusual processes must be initiated in shock compression. Chief among the unique shock processes is the mixing of reactants by the large kinetic energy of shock-compression pulses. Mixing and fluid-like flow can lead to sufficiently intimate contact between reactants to permit complete chemical reaction in the solid state on the time scale of the experiment. Shock-induced solid state chemistry may be described as an unusually intense mechanochemical process.

INTRODUCTION

There have been many reports of chemical synthesis of compounds from reactants in the form of mixed powders which have been subjected to high pressure shock compression (1). To the extent that such reports indicate that chemical reaction can occur between solids or between solids and partially melted solids while in the shock-compressed state, very significant questions are raised concerning our understanding of details of the shock-compression process and shock-compressed materials. Indeed, shock-induced solid state chemistry is a major neglected area of shock-compression science with the prospect of providing significant new insights into the shock-compression process.

At the time of the first reported compound synthesis from mixed powders by Kimura in 1963 (2) there was insufficient knowledge of mechanical and physical processes in shock-compressed solids to judge the credibility of the limited observations. Over the next twenty years considerable knowledge of shock-compression processes in solids and powder compacts has been developed and a number of detailed studies of chemical synthesis and of residual properties of shock-compressed samples have been carried out. Further, development of realistic computer codes for numerical simulation provided the capability for description of shock-compression signatures to be determined in samples in which chemical changes are encountered. Given the newer developments, the best evidence indicates that not only do

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chemical processes occur frequently during shock compression events, but that we should, in general, expect them to occur.

The question of shock-induced solid state chemical change is, in itself, a difficult question, but equally difficult is a description of compression processes encountered in the highly porous, powder compacts in which such reactions are typically observed. Further, many reactants are brittle inorganic materials whose deformation behavior is not well studied under high pressure, shock compression. Thus, the chemical issues cannot be divorced from the porous powder-compact issues.

In the present paper some of the critical issues involved in descriptions of shock-induced solid state chemistry will be reviewed. It will particularly emphasized that the critical processes are basically mechanical in character and that without a realistic treatment of the mechanical features, the underlying chemical issues cannot be addressed.

BASIC QUESTIONS IN SHOCK-INDUCED SOLID STATE CHEMISTRY

Fluid-Like Flow in Shock-Compressed Solids

In much of shock-compression science the distinction between solids and fluids is blurred. The oft-applied assumption that at pressures much greater than the Hugoniot elastic limit the strength of the solid can be ignored leads to analyses of high pressure shock waves in which solids are treated as fluids as far as material flow is concerned. The neglect of strength may be an excellent assumption in terms of the stress tensor, but it does not wipe away the basic questions of high speed deformation in solids. The observed fluid-like flow is, in itself, direct evidence for the dramatic transformation which must occur in solids in the shock transition. Defects must be initiated and moved under the high shear stress in the transition to decouple the deformation from the lattice forces characteristic of deformation of solids. Thus, the first-order observation of fluid-like flow in shock-compressed solids requires recognition of defect processes which are thermomechanical and heterogeneous in character. Lower elastic limits indicate more plastic deformation at lower stresses, not less influence of solid behavior.

Once it is recognized that shock compression is a deformation process involving plastic deformation, fundamental studies must address its consequences. The consequences are not thought to be severe if the end result of the a study is to define the shock pressure at a particular volume compression or to determine the shock speed at a particular macroscopic mass velocity. Other problems, especially chemical ones, require deeper inquiry into the influence of defects and there is considerable work in conventional solid state chemistry to guide our efforts under shock compression.

Although there is a tendency to try to develop an understanding of shock-induced chemical effects in starting solid materials in terms of liquid-phase chemistry, it is clear that the basic issues, which involve explicit treatment of the defect solid state, are ignored with this approach. The wrong questions are asked by forcing liquid concepts on a solid phase problem, and the answers achieved are inevitably unrevealing of the process.

Conventional Solid State Chemistry

At the beginning of the 20th century it was the established view that chemical change was characteristic of fluids, not solids. Hedval (3) has called attention to the difficulties in accomodating views of solid state chemistry into the then-existing chemical sciences. Solid state chemistry is now a well established discipline and the influences and properties controlling solid state reaction are well established. Texts by Schmalzried (4) and West (5) are excellent sources which can be consulted for established views. For pyrotechnics, McLain (6) emphasizes the role of solid state chemistry in energetic reactions.

As is clear from the texts above, solid state chemistry is distinctive from chemistry in liquids and gases. In the liquid and gas state, reactivity depends on bulk properties. In the solid state, reactivity depends upon deviations from bulk properties. This qualitative difference arises from the very limited atomic diffusion possible in solids. As the defects in solids control the kinetics, solid-liquid and solid-gas reactions involve explicit treatment and control by solid state chemical processes. Thus, in solids, defects--from atomic to macroscopic--determine solid state reactivity and are the vehicle for chemical change. Their characteristics are the basis for both theory and experimentation in the area.

To characterize these defects, a wide variety of materials probes, common to solid state physics and materials science, are typically employed. Those which are the most widely used are shown in Figure 1. As shown, there are a wide variety of probes that reveal various aspects of defects.

SCHMALZREID - WEST

SOLID STATE CHEMISTRY - USUALLY INORGANICS
DEFECTS, MICRO STRUCTURE - FIRST-ORDER INFLUENCE
ON KINETICS / REACTIVITY

DOMINANT PROBES -
- STRUCTURE
  - X-RAY DIFFRACTION
  - ELECTRON DIFFRACTION
- DEFECTS
  - LINE BROADENING
  - ELECTRON SPIN RESONANCE
  - MOSSBAUER SPECTROSCOPY
- MICROSTRUCTURE
  - OPTICAL MICROSCOPY
  - ELECTRON MICROSCOPY
- MORPHOLOGY
  - OPTICAL MICROSCOPY
  - BET SPECIFIC SURFACE
- SOLID STATE REACTION
  - THERMAL ANALYSIS

Figure 1. Conventional solid state chemistry studies as described by Schmalzreid and West utilize a variety of material probes.

The probes listed in Figure 1 are widely available in the materials science and solid state physics laboratories but require scientists in charge of interpretation of the results and design of the materials analysis experiment.

None of these solid state probes are available for use under the transient conditions of high pressure shock-compression loading. Further, its is also important to note that conventional optical spectroscopy has not proven to be a mainstream tool in solid state chemistry. Such spectroscopy is most revealing of bulk properties but is limited as to the information provided about defects.

Basic Issues in Shock-Induced Solid State Chemistry

Given what is known about high pressure shock-compression processes in powder compacts and conventional solid state chemistry, the issues to be addressed in shock-induced solid state chemistry are well defined.

> First, the relation between shock compression conditions and defect structures from atomic to microstructural must be studied. As different materials characterization techniques yield information on different defects, an array of probes must be employed. Many of the materials to be studied are considered to be brittle under conventional loading, and, unlike metals, they are especially in need of characterization.
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> Second, the extent to which the shock-compression enhances solid state reactivity must be investigated. The relation between defect structure and density and solid state reactivity must be quantified.
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> Third, controlled shock-induced solid state reactions must be studied over a range of shock conditions. Samples shock-compressed at conditions just prior to reaction are especially revealing of the basic mechanisms.
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> Because of the importance of the shock consolidation (compaction) process, data on changes in the morphology of powder compacts at various stages of compaction over a range of shock conditions need to be defined.
>
> As in any scientific endeavor, it is essential to quantify the excitation conditions--the overall pressure-versus-time and mean bulk temperature-versus-time signature. This endeavor requires realistic, two-dimensional numerical simulation.
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> Rather than limiting the studies to a few selected materials, the lack of fundamental basis for modeling and developing a theory for shock-induced solid state chemistry requires the study of a large number of materials.

STUDIES IN SHOCK-INDUCED SOLID STATE CHEMISTRY

There have been a number of reviews published over the past few years. A comprehensive bibliography of work prior to 1980 (7) was followed by the review of Morosin and Graham (8) which provided some interpretation of that work. Recent work at our laboratories is reviewed by Graham and coworkers (9,10). A comprehensive source of much of the data obtained in various laboratories is collected in the book by Graham and Sawaoka (11).

Residual Properties-Shock Modification

X-ray diffraction line broadening studies of shock-modified powder compacts have been carried in greater depth and breadth than with any other materials probe and perhaps give the clearest picture of the overall defect condition in the samples. The work is summarized in various publications by Morosin and coworkers (12-15). It is to be recognized that analysis of line-broadening in typical shock-modified materials has required a significant extension in the state of the art in analysis of line-broadened diffraction patterns. The newer developments arise because most of line-broadening theory and practice have developed around metals which are cubic in structure. Most of the materials of the present study are brittle refractory materials in which plastic deformation is not usually encountered and are of lower crystallographic symmetry. Furthermore, the shock-modified samples typically exhibit anisotropy in broadening--the deformation is not uniform along different crystallographic directions. It is also observed that line broadening is caused by both residual strain and reduced crystallite size. Separating the two contributions requires careful, detailed study.

Detailed studies have been carried out on titanium carbide, titanium dioxide, aluminum oxide, hematite and lanthanum hexaboride. Less detailed work is reported in aluminide nitride, titanium diboride and silicon nitride.

Each material behaves differently, but all exhibit common important features. In every case the amount of residual strain present is characteristic of plastic deformation to levels such as those achieved in cold-worked metals. What is different in different materials is the threshold to achieve significant residual strain and the pressure level to achieve a saturated level of residual strain.

Line broadening reveals that the coherent crystallite size is significantly decreased with increasing shock pressure. The reduced crystallites typically achieve values of hundreds of angstroms. In this size range, surface effects can become large and contribute significantly to chemical reactions. Such crystallite sizes have been termed "mesoscopic" and unusual physical properties are reported in the size range less than a few hundred angstroms.

Electron spin resonance has proven to provide a detailed picture of point defects in rutile (16). Point defect concentrations are typically observed to increase in shock-modified powders. Identification of the particular defect and its concentration requires detailed study which has only been carried out in rutile. In that material, it was found that two paramagnetic resonances were produced by the shock process. An isotropic resonance can be identified as due to electrons trapped at vacancies and an anisotropic resonance can be identified as intersititial titanium with a reduced valence. The titanium interstial was found in concentrations an order of magnitude larger than achieved in other defect studies.

Analytical electron microscopy has been able to identify specific defect structures (17). Typically, their concentrations are too large to quantify in TEM studies. Scanning electron microscopy and electron diffraction shows the very substantial changes in particle morphology produced in shock-modified powders as they are compressed to solid density.

In magnetic materials, static and dynamic magnetization measurements and Mössbauer spectroscopy are sensitive probes of shock-induced defect configurations. The work on shock-modified hematite (18) has provided a revealing picture of atomic-level consequences of shock-processing.

Residual Properties-Shock Activation

The unusually high defect concentrations resulting from high pressure shock modification would be expected to cause greatly enhanced solid state reactivity. It is necessary to quantify various manifestations of enhanced reactivity as the defect concentrations and configurations are not encountered in any other process. In work at our laboratory, enhanced reactivity has been studied in catalytic activity of rutile and zinc oxide, dissolution rate of silicon nitride, structural transformation temperature of zirconia, enhanced consolidation rates in hot-pressed aluminum nitride and titanium carbide, greatly enhanced kinetics for the theta-to-alpha transformation in alumina (1,10) enhanced dissolution rates of rutile (19) and other minerals (20).

What is generally observed in the shock-activation studies is an enhancement of solid state reactivity by many orders of magnitude. The observed changes show that the shock compression event incorporates processes that will strongly affect rates of chemical conversion. In addition to enhanced solid state reactivity, the mechanical deformation acts to remove surface contaminants which typically strongly impede chemical kinetics.

Residual Properties-Chemical Synthesis in Mixed Powders

Three model material systems have studied in work at our laboratory. Synthesis of zinc ferrite from mechanical mixtures of zinc oxide and hematite was carried out as a typical solid state reaction with a modest heat of reaction. Synthesis of aluminides from mechanical mixtures and composite particles of nickel and aluminum and titanium and aluminum was carried out as a system which is well studied under more conventional synthesis processes and one with a strong heat of reaction. In recent unpublished work, the classical thermite reaction involving mechanical mixtures of aluminum and hematite has been studied as a typical solid state reaction with a very large heat of reaction.

In all of these cases, samples were obtained for shock-compression conditions in which reaction was incipient so that the conditions which exist when reaction is actually initiated can be evaluated.

Submicrosecond Observations

The fundamental question raised by shock-induced solid state chemistry cannot be directly addressed by measurements on samples while they are under the action of the shock-compression event, but such measurements can be used as an overall indication of the consequences of the reactions. The pyrometric measurements of Boslough (21) have shown clear evidence for reaction on time scales of hundreds of nanoseconds but, it has proven difficult to distinguish between bulk chemistry and localized spurius effects. Perhaps the most significant conclusion from that work is the thermochemical modeling which shows the character of the reaction to be one in which the resulting pressures are little affected by the reaction. The process produces very high temperatures, but little increase in pressure.

Boslough's observation shows that wave profile measurements can be used to show the existence of reaction, but can provide only an approximate indication of the basic thermochemical consequences.

Wave profile measurements in shock-compressed mixed powders have been reported by Kovalenko and Ivanov (22), Sheffield and Schwartz (23) and Batsanov and coworkers (24). Evidence for chemical reaction on a time scale of tens of nanoseconds is shown in the data.

SHOCK-COMPRESSION PROCESSES FOR CHEMICAL REACTION

Based on the studies presented above, an overall picture of the shock-compression processes critical to the understanding of shock-induced solid state chemistry can be identified. These processes are summarized in the cartoon of Figure 2. In the figure, time at a given location progresses from the bottom to the top. The initial configuration has a strong influence on the resulting processes principally through the control it exercises on energy localization and subsequent mass mixing. The transition zone represents the space over which the pressure is increased to a peak value. The time involved in the transition zone will depend strongly on the particular shock-loading conditions but can vary from a few to hundreds of nanoseconds. Within the transition zone, very large gradients in particle

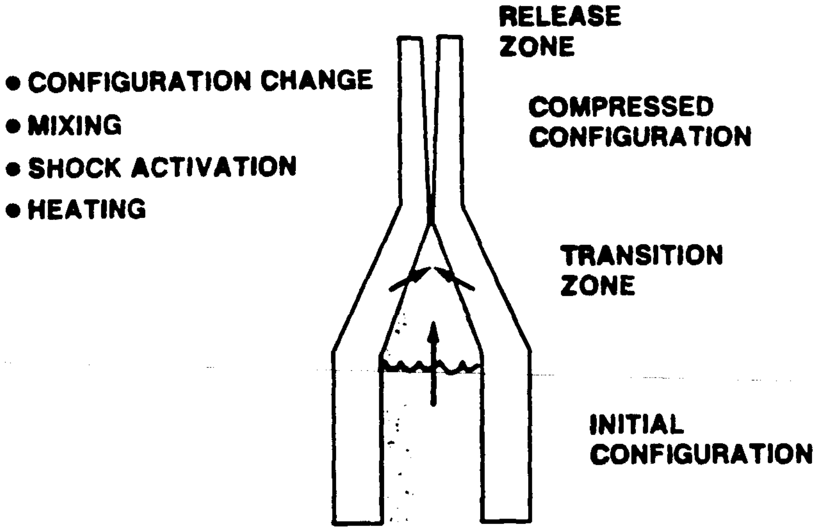

Figure 2. Critical considerations involved in shock-induced solid state chemistry are depicted in the cartoon. The processes are critically affected by the initial configuration and the transition zone. Shock-induced mixing in the transition zone is thought to be the most critical process.

velocity and localization of kinetic energy are achieved. In the compressed configuration, a quasistable configuration is achieved in which the pressure, particle velocity and temperature are nominally constant. In this region changes in conditions are more likely to be controlled by kinetics of reactions than by the driving shock conditions. Finally, the release zone accomodates the reduction in pressure and temperature. The release region is characterized by large gradients in particle velocity, but the release is from a solid, shock-modified state rather than from a highly porous state or initial unstressed state. In such a dense state, mixing is more limited than in the porous state.

Perhaps the most critical region is the transition zone whose principal features are indicated in the upper left side of the figure. It is important to recognize that the shock-compression process causes irreversible changes in the starting configuration such that at the time chemical reaction is initiated the configuration is substantially altered. In a porous solid, individual particles are substantially deformed to fill the voids. The local deformation of the particles is strongly influenced by the morphology and the starting density. In a solid density sample the defect configuration is substantially changed from the atomic level to microscopic level in the transition region.

The mass mixing that occurs during the transition zone is thought to be the most critical process affecting subsequent chemistry. In a porous sample, the pores act to localize the kinetic energy and provide a space in which reactants can mix. The mixing made possible by the pores is thought to provide the principal difference between chemistry in porous and solid density samples. In the fully dense solid state, the range over which mixing can occur is restricted.

As the individual particles are deformed, the solid state reactivity is greatly enhanced and impurities are removed from their surfaces. This shock-activation process provides reactants which are much more favorable for subsequent reaction.

Finally, heating, either localized or uniform provides the thermal environment required to initiate reaction is mixing is sufficient and activation has enhanced the reaction kinetics. Although the shock-induced temperature is essential for reaction to proceed, the typical temperatures achieved in shock-compressed powder compacts at relatively modest pressures are sufficient for solid state reactions to proceed.

CONCLUSIONS

With considerable concentrated work over the past ten years, an overall picture of processes important for an understanding of shock-induced solid state chemistry is beginning to emerge. The scientific aspects of the problem are very different from traditional shock-compression science. These differences make it difficult to develop appropriate models of the processes. These differences require that we develop a much more detailed picture of shock compression at the atomic and microscopic level than has heretofore been possible.

In describing shock-induced solid state chemical processes, the defect state and heterogeneous nature of shock compression are of first-order importance. Thus, we need to develop a much improved understanding of shock compression as a "catastrophic shock" process based on a defect solid under heterogeneous, nonequilibrium conditions rather than the traditional "benign shock approximation" description of a perfect, fluid-like solid in thermodynamic equilibrium usually employed.

The substantially different questions raised by studies of shock-induced solid state chemistry promise to provide a more detailed, realistic picture than that resulting from the mechanical and physical considerations with which we are so familiar. Indeed, the challenge is to develop a fully integrated, mechanical-physical-chemical picture of the shock-compression process. The development of such descriptions will require us to critically examine favorite, established experimentation and theory in favor of approaches which address the issues described in the present paper.

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