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A New Experimental Approach
to Study Solid Combustion Reactions
Using Synchrotron Radiation

J. B. Holt
Joe Wong
E. Larson
P. Waide
B. Rupp
R. Frahm

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**A New Experimental Approach
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J. B. Holt, Joe Wong, E. Larson, P. Waide, B. Rupp, and R. Frahm

We have recently utilized the high intensity characteristic of synchrotron radiation and performed a series of proof-of-principle time-resolved x-ray diffraction (TRXRD) experiments at the Brookhaven National Synchrotron Light Source to follow the phase transformations in a number of solid combustion systems in-situ at high temperature. A photo-diode array (Princeton Instrument) which is capable of recording a full scan of 1024 pixels in 4 msec, was used as a position-sensitive detector to record the TR-diffraction patterns from the reacting specimen situated in a specially designed reaction chamber-diffractometer with a vertical θ - 2θ geometry.

The systems thus far studied include:

- 1) $Ti + C = TiC$
- 2) $Ti + C + xNi = TiC + xNi$
- 3) $Al + Ni = AlNi$

In the latter reaction, we were able to achieve a time resolution of 20 msec. and record the formation of pre-reactive phases, melting of the reactants, reaction intermediates and final products in a total scan time of two minutes.

These synchrotron experiments open a new route to study the chemical dynamics and phase transformation of reactive systems in-situ, at high temperature and under other external perturbations in the time domain of a few milliseconds which has not been possible before.

KEYWORDS: *Synchrotron radiation, time-resolved x-ray diffraction, intermediate phases, composites, Nickel aluminide (NiAl), Titanium Carbide (TiC), combustion synthesis, intermetallics**

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1. Introduction

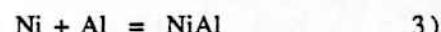
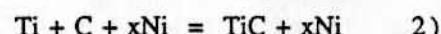
Combustion of gaseous reactants has been actively studied for many years. However, there is a type of combustion, where at least one of the reactants is a solid, which has received little attention from material scientists. The product(s) of these "solid flames" are technologically important materials such as ceramics, intermetallics, and composites. The name applied to the combustion process involving solid reactants is Self-Propagating High Temperature Synthesis (SHS) or simply Solid Combustion Synthesis (SCS). Although the basic concepts of this method of material synthesis are relatively easy to apply in principle there remain many questions concerning the nature of chemical reactions and dynamics of phase transformations at the combustion wave front. This situation is true with even the most "simple" combustion reactions. To fully exploit the use of combustion reactions to process materials basic mechanisms must be identified. Some of the crucial issues are: the role of liquid formation, the effect of intermediate or transient phases on the combustion process, the factors influencing the microstructure of the products, and the different stages of reaction. The main obstacles in obtaining basic data are the high self-generated temperatures (800 -3500 C) and rapid reaction times (0.1-15 cm/s).

Recent research (1-3) has provided evidence that it is now possible to observe in real time the dynamic changes occurring at the combustion front and "afterburn" region by a more direct method of measurement. By using an intense source of synchrotron radiation (10^{10} photons/sec.), and a position-sensitive photo diode array detector, we have shown that time-resolved x-ray diffraction (TRXRD) patterns can be taken of the combustion reactions down to 20 msec., in the case of the Ni-Al system. In the future this scan time may be reduced even further by refinement of the equipment and experimental procedures, and by the use of a more intense radiation source (10^{12} photons/sec). Simultaneous measurement of wave velocity and temperature profile, along with TRXRD permits the different phases to be determined as a function of time and temperature. This novel experimental approach

will provide basic information about fast chemical reactions that is impossible to obtain with other indirect and postmortem techniques. This paper reports the results of our first series of experimental runs carried out at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

2. Experimental Procedures

The reactions shown in the following equations were selected as the model combustion systems to use in the development of the experimental procedures .



The selection of these reactions was based on the relatively large volume of experimental data already available on their combustion behavior (4-8)*. In addition the products of reactions 1), 2), and 3), are representatives of a ceramic, composite and intermetallic material respectively.

The as-received powders were dry mixed in either a shaker or ball mill for periods of time up to 2 hours. The titanium powder had a average particle size of approximately 10μ , while the aluminum powder was 5μ in size. The nickel powder had an average particle size of 20μ . Both amorphous and graphite carbon powders were used in these preliminary experiments. The amorphous carbon was submicron and more active than the graphite carbon. Preparatory combustion reactions were performed to evaluate the degree of sample expansion versus the type of carbon powder. Expansion of the combustion product is due to the evolution of gases absorbed on the reactant powders. It was found that a Monarch 900 carbon black from Cabot Corp. caused the least mount of expansion (6%). Therefore, in reactions 1) and 2) we used the Monarch 900 carbon to minimize the vertical

*This does not represent a complete list of reports on the combustion reactions designated as model systems.

movement of the combustion surface. To eliminate density as a variable all samples were cold-pressed without any binders to densities of $55 \pm 1\%$. Typically, the samples were in the shape of cubes 1.9 cm. on edge.

Figure 1 is a schematic diagram of the chamber used for the combustion experiments on beamline X-11A at NSLS. The monochromatic radiation beam enters the chamber from the right through a thin mylar window.

It impinges on the surface of a sample of cold-pressed mixed powders held in a stainless steel attachment. The diffracted beam passes through another mylar window where it is recorded by a Princeton Instrument solid state detector consisting of a photo-diode array of 1024 pixels located on the outside circumference of the chamber. The preselected 2θ angle is set by rotation of the detector and sample holder to the proper position by computer control. A W-Re thermocouple is inserted into the sample through a hole drilled into the side. This thermocouple is located forward of the spot where the beam strikes the surface and is used to trigger the detector. A second thermocouple is located directly below where the beam hits the surface. The signal from this thermocouple is used to measure the temperature profile. The wave velocity is determined by measuring the time to traverse the known distance between thermocouples. It is also possible to measure the velocity with a video camera.

When the sample is loaded, then the chamber is pumped down and backfilled with helium to a pressure of 0.5 atmospheres. The cold-pressed sample of reactant powders is ignited with a heated tungsten coil. The detector is triggered when the thermocouple nearest to the advancing combustion front reaches a pre-selected temperature such as 1,000 C. The diffraction peaks in the 60° of 2θ space are recorded at a set scan rate and total scan time on a IBM computer. Since the time between scans is in the range of microseconds there is essentially no dead time between scans.

3. Experimental Results

Figure 2 displays the data from one experiment with combustion reaction 2). Each of

the 200 scans took 200 msec. so that the total scan time was 40 seconds. From the 200 scans 6 representative scans were chosen to demonstrate the sequence of events during combustion. The bottom scan at zero time shows the Ti(101) line. In the next scan at 2.4 seconds the titanium peak has disappeared because the titanium has melted and the (200) diffraction peak of the TiC product phase appears. Between 2.4 and 2.8 seconds the TiC peak grows until the TiC phase is completely formed by 2.8 seconds. The next three scans show the TiC 200 peak moving to the right indicating a contraction in d-spacing caused by the cooling of the TiC. From this sequence of x-ray diffraction scans we learn that the first step in the combustion process is the melting of titanium particles. Subsequently, the molten titanium reacts with the solid carbon particles. It has been suggested (3) that the mechanism of reaction is one of solution-precipitation rather than solid state diffusion through a growing TiC layer. In this mechanism the carbon dissolves in the molten titanium and then precipitates out as TiC grains which grow in size with time. The total reaction time for the complete formation of TiC is less than 0.5 seconds. Furthermore, there is no evidence of the formation of intermediate phases. In a separate experiment with the same reactants the detector was moved to a new position in order to monitor the change in the Ni(111) peak and the Ti(102) peak. Within 3.6 seconds both the titanium and nickel have melted and at 3.8 seconds we see the appearance of the (202) peak of the intermetallic compound Ni_3Ti as shown in Figure 3). This peak grows and moves to the right as this phase cools down. An unknown intermediate phase is observed for about 8 seconds. The final products of combustion reaction 2) were TiC and Ni_3Ti .

Although we conducted only a few experiments with combustion reaction 3), these preliminary results show a complicated sequence of events in the synthesis of the NiAl combustion product. In Figure 4a, the bottom scan at zero time clearly shows the Ni(111) peak with the smaller Al(202) peak on its shoulder. The scan at 0.3 sec shows two peaks attributed to nickel. The beam width is approximately 1 mm when it leaves the collimator. Since it strikes the surface at a oblique angle then the width of the irradiated line is nearly 2.6 mm. For this reason we observe hot nickel in the combustion front

(peak on the left) and the nickel still at room temperature. Since the coefficient of thermal expansion for nickel is known then the temperature may be determined by measuring the change in d-spacing. The temperature at that point in the reaction is about 1300 C. At 0.4 seconds we see only one peak for nickel which has moved further to the left as the temperature of the nickel continues to rise. By 0.7 seconds the nickel has melted and several small sharp peaks cluster together which suggest the existence of crystallites of different orientation in the molten nickel. After the nickel melts there is a period of nearly 8 seconds before we see the peaks of an unknown intermediate phase. An intermediate phase in this context is defined by diffraction peaks that we observe to appear, grow, shrink and finally disappear. Thus, they are present for short intervals of time during the reaction. We also note that the measured velocity of the combustion front is about 1.0 cm./sec. for reaction 3). This fact points out that the front has already passed through the reactants and the appearance of the intermediate phases occur in the "afterburn" region. Figure 4b shows the appearance of three more intermediate phases. The peak for the NiAl product does not appear for about 30 seconds. Then it moves to the right as the product cools down. The intermediate phases are characterized by sharp peaks suggesting crystallites in a molten medium. So far none of the intermediate phases have been identified as one of the known equilibrium phases present in the phase diagram. The long "afterburn" region is consistent with the visual observation of the brightness of the burned sample being sustained for almost one minute. These results raised questions that will be examined in our second group of experiments that took place at Brookhaven in December. Experiments were set up to establish reproducibility, the exact number of intermediate phases, the identity of these unknown phases, and the effect of lowering the temperature below the melting point of nickel. Other Ni-Al equilibrium phases will sustain self-propagating reactions, such as AlNi_3 , Al_3Ni_2 , Al_3Ni_5 , and AlNi_3 . The TRXRD data from each of these systems is now being analyzed and will be reported elsewhere.

4. Summary

Our experimental findings may be summarized as follows:

1) In the $\text{Ti} + \text{C}$ reaction we showed that the first step is the melting of the titanium metal. The melting takes place within 200 msec. or less. TiC is the final product and there is no evidence of any intermediate phases.

2) In the $\text{Ti} + \text{C} + 25 \text{ wt.\% Ni}$ reaction the first step is the melting of both the nickel and titanium. The temperature is lower and the product stays at higher temperatures for longer periods of time than the preceding reaction. An intermediate unknown phase coexists with Ni_3Ti for nearly 8 seconds while the final products are TiC and Ni_3Ti .

3) The most interesting and complicated of the three reactions was 3), the synthesis of $\text{Ni}+\text{Al}$. Again the combustion temperature is higher than the melting point of either Al or Ni so that the first step in the reaction is the melting of the reactant metals. After the melt, four unknown intermediate phases appear in sequence. The NiAl product does not appear until 30 seconds after the passage of the combustion front. The final product is NiAl.

Therefore, we have demonstrated with these first experiments that the use of time-resolved x-ray diffraction using synchrotron radiation is a powerful method to follow phase transformations and chemical dynamics of solid combustion reactions in-situ at high temperatures. When this data is correlated with wave velocity and temperature profile measurements then all participating phases may be identified as a function of time and temperature. This intrinsic kinetic data will allow existing theoretical models to be examined and may suggest that new ones need to be developed.

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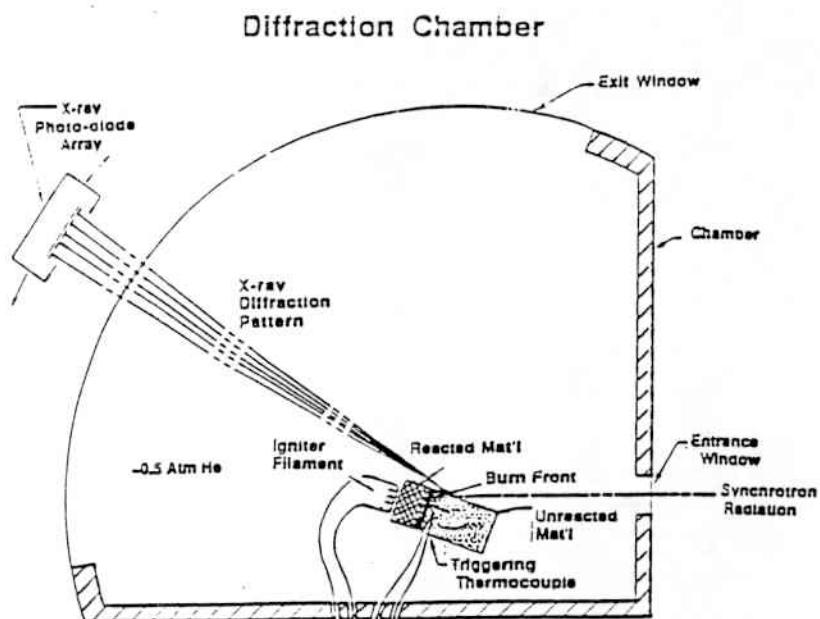


Figure 1. Schematic drawing of diffraction chamber that is used in the combustion experiments at synchrotron radiation light source at Brookhaven National Laboratory.

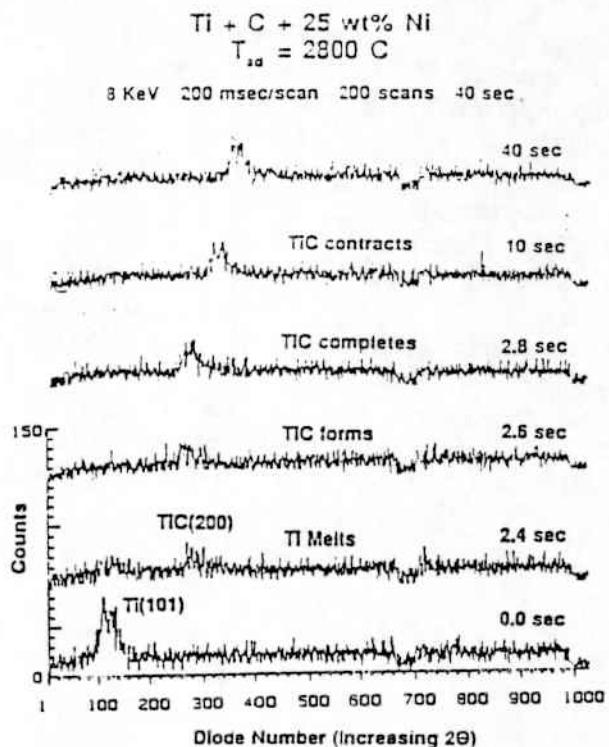


Figure 2. Selected time-resolved diffraction scans showing the sequence of events in combustion reaction 2).

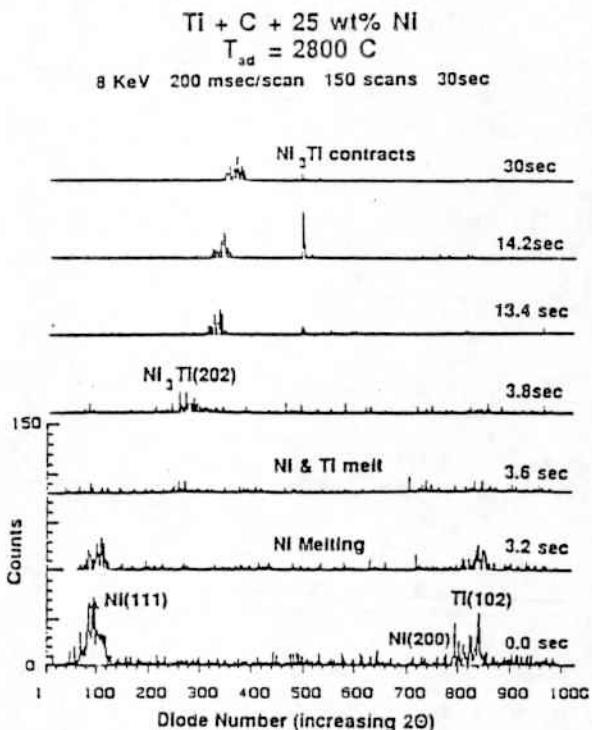


Figure 3. Scans of the same reaction as in Figure 2 but following the Ni(111) and Ti(102) peaks and the growth of the Ni₃Ti product.

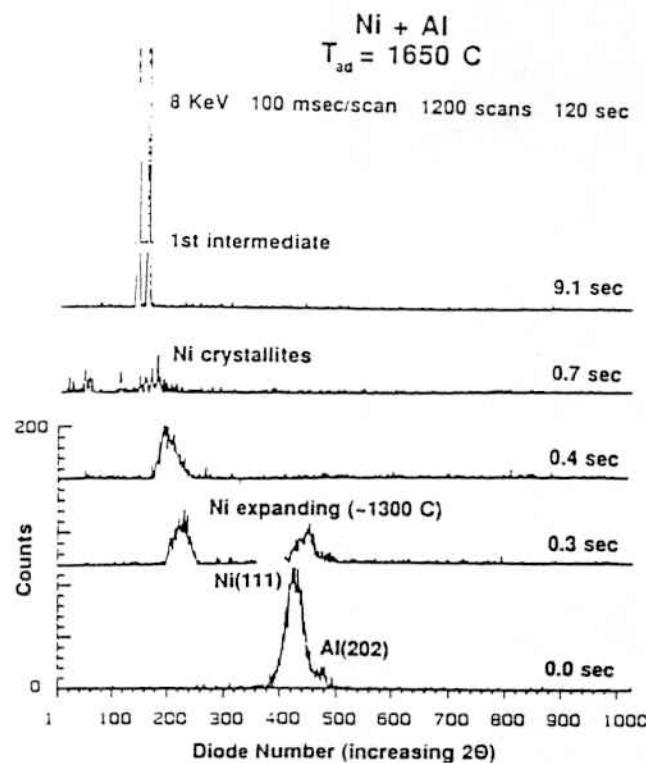


Figure 4a. X-ray diffraction scans at 100 msec/scan taken of reaction 3) showing the melting of the nickel and the appearance of the 1st intermediate phase.

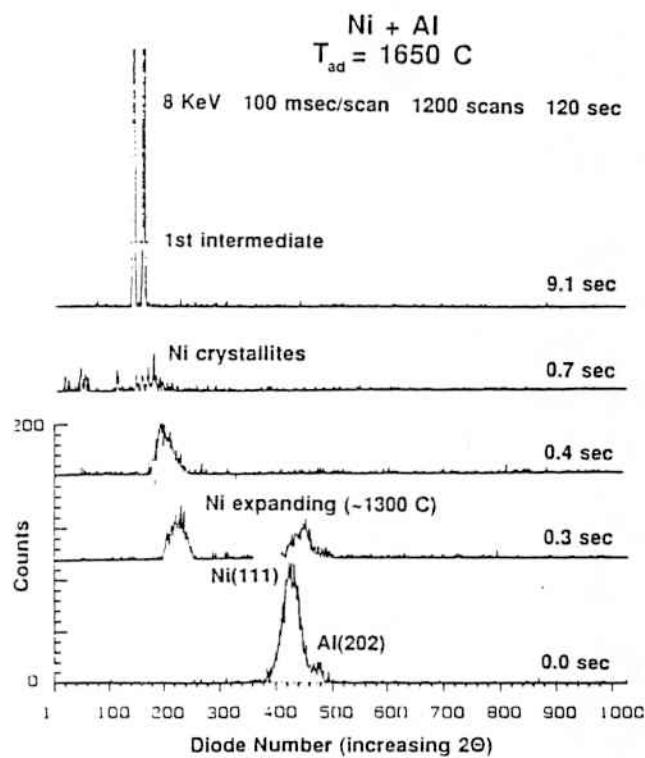


Figure 4b. A continuation of scans of the same reaction shown in Figure 4a.