

The study of Ni + Al self-propagating high-temperature synthesis using synchrotron radiation and a two-dimensional DED-5 detector†

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New kinetics data have been obtained for a Ni + Al self-propagating high-temperature synthesis (SHS). In order to achieve a time resolution of 0.005 s it was necessary to increase the intensity of the incident beam and the aperture of the X-ray detector. A graphite monochromator with a wavelength bandwidth of $\Delta\lambda/\lambda \simeq 10^{-2}$, instead of the traditional 10^{-3} – 10^{-4} , and a two-dimensional detector (DED-5) were used for these purposes. Analysis of the kinetics data indicated that the main chemical transformations occurred during 60–70 ms. The DED-5 detector also helped to establish that the recrystallization process of intermetallide NiAl took place some time after the SHS, and the formation of crystallites could be seen as separate Bragg spots on the detector image.

Keywords: self-propagating high-temperature synthesis; kinetics.

1. Introduction

The first experimental data for self-propagating high-temperature synthesis (SHS) were obtained about 20 years ago in Novosibirsk (Boldyrev *et al.*, 1981; Aleksandrov *et al.*, 1983; Merzhanov, 1990). A one-dimensional OD-2 detector was used and a frame time (exposure

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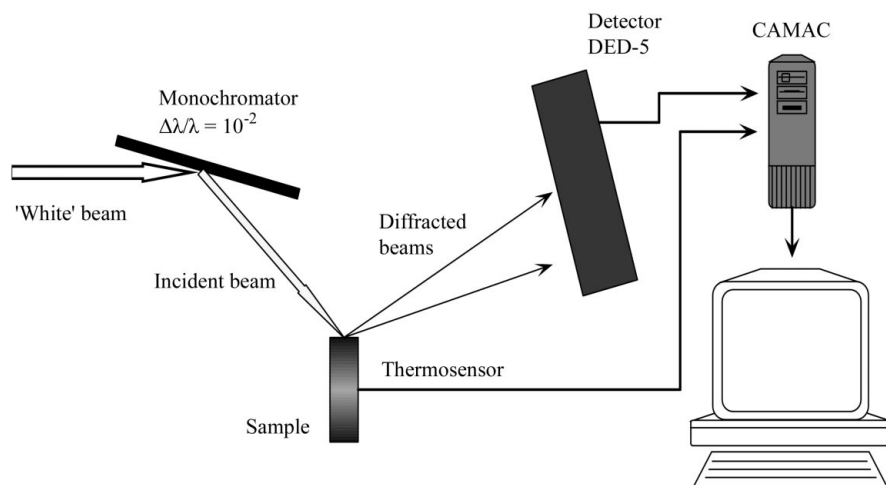


Figure 1
Experimental layout.

time) of about 1 s could be achieved. The study was continued at other synchrotron radiation sources: NSLS-II (Wong *et al.*, 1990; Holt *et al.*, 1990), LURE (Held, Gras *et al.*, 2000; Held, Vrel *et al.*, 2000; Bernard *et al.*, 2000) and ESRF (Curfs *et al.*, 2000). The method was developed mainly by using two-dimensional detectors adjusted to two different diffraction regions and infrared cameras for temperature measurement. The achieved frame time was less than 60 ms for the ESRF experiments. High-speed photography showed that the reaction between particles in the powder mixture occurs during ~ 0.001 s. Here, we report our work using a DED-5 detector (Baru *et al.*, 1997).

2. Experimental

In the previous investigations, the traditional scheme was used, where a monochromatic synchrotron radiation beam is incident on the lateral face of the sample, perpendicular to the reaction front. The registration zone had a width of ~ 1 mm and a height of a few mm in the first experiments, and down to 0.2 mm \times 0.2 mm for experiments performed at the ESRF. Thus, a few problems were experienced during some of these experiments:

(i) The increase in spatial resolution (*i.e.* decreasing of registration zone width) leads to a decrease of the intensity of the diffracted beam.

(ii) Use of a one-dimensional detectors only allows the collection of a few percent of the full diffraction cone, resulting in low quality of the obtained data owing to counting statistics and errors owing to the occurrence of inhomogeneous powder patterns.

(iii) One-dimensional detectors do not allow observation of the evolution of the reaction products due to the aperture being too small, as will be shown below.

In this paper we present an experimental scheme that addresses some of these problems. The scheme is presented in Fig. 1. Since a one-frame exposure time is very small, some improvements have been made to obtain suitable data:

(i) We used a graphite monochromator, which gives a wavelength bandwidth of $\Delta\lambda/\lambda \simeq 10^{-2}$ instead of the traditional $\Delta\lambda/\lambda = 10^{-3}$ – 10^{-4} obtained using Si or Ge monochromators. Thus, the intensity of the incident beam was increased by up to ~ 100 times.

(ii) The two-dimensional DED-5 gas detector allowed a significant increase of the aperture (*i.e.* amount) of registered photons. It had a 384 mm \times 384 mm working area with a spatial resolution of 1.5 mm \times 1.5 mm. The dead time (the time required to read the data) was 10 μ s. This detector also allowed observation of the behavior of the reaction products.

(iii) The sample was placed vertically so that the reaction front was parallel to the registration zone.

The wavelength was 1.54 Å and a slit system formed a registration zone of approximately 2 mm \times 2 mm (projected). The sample powders were Ni (electrolytic, 99.5% purity) and Al (99% purity) with particle sizes of less than 100 μ m. As shown in the REM (reflective electron microscopy) images, the particles were mostly spherical with a size distribution of 10–50 μ m. The sample was a 10 mm \times 7 mm \times 20 mm parallelepiped of Ni + Al (1:1), pressed to a relative density of 0.5–0.6. The sample was ignited from below. When the combustion front reached the thermosensor it triggered

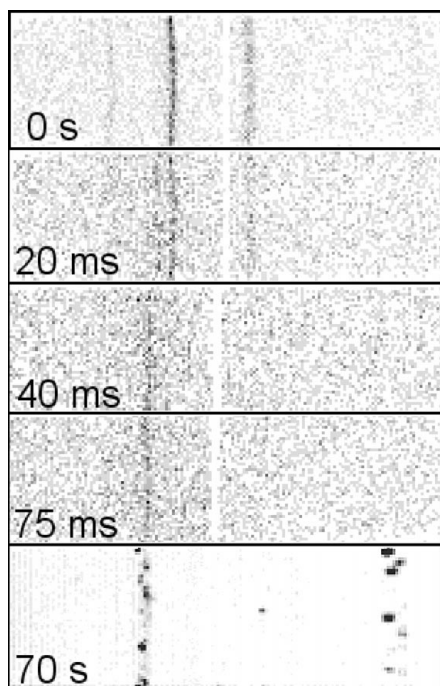


Figure 2
Experimental data from the detector DED-5.

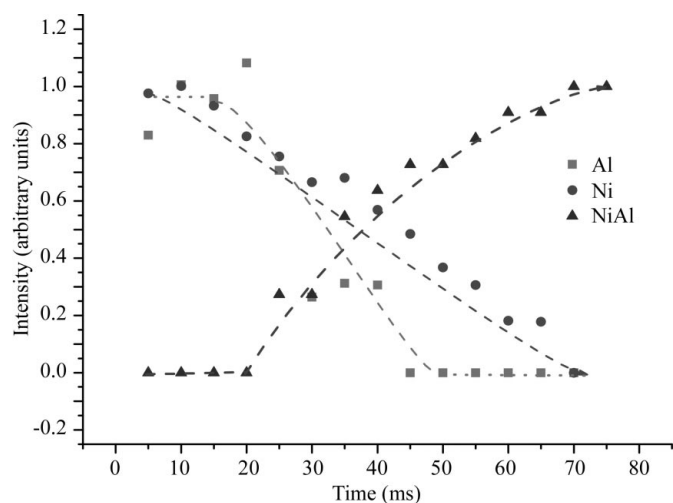


Figure 3
The treated kinetics data for the Ni + Al system.

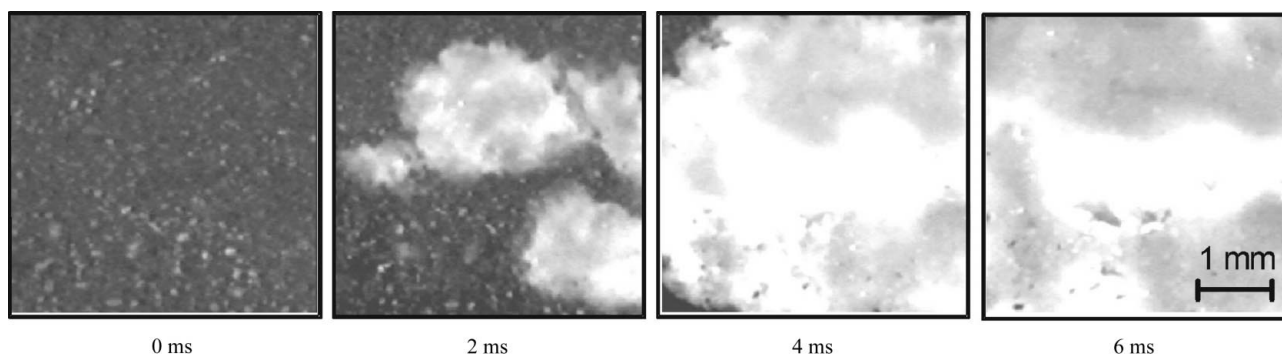


Figure 4
Frames from a high-speed video of the combustion front at the top of the sample.

the DED-5 detector. The detector was started in continuous 'cinema' mode, where a given number of frames with given exposure time were recorded. Each separate frame time was 5 ms and there were 300 frames. Approximately 60–70 s after the end of the first recording sequence a few one-frame exposures were recorded to obtain information about the products.

3. Results and discussion

The mechanism of the interaction between Ni and Al during SHS has been discussed for a long time, and, in particular, the formation of intermediate phases has been of interest. The data obtained here provides an opportunity to address this. The experimental data from the detector at a few time intervals of the reaction are shown in Fig. 2. Fig. 3 represents the kinetics curves of the initial and product substances. The points on the curves were calculated by integrating along corresponding arcs using specially developed software.

It should be noted that the combustion front for gasless systems due to heterogeneity is not ideal and might lead to incorrect results. To estimate these errors, a high-speed video ($500 \text{ frames s}^{-1}$) was recorded when the combustion front was arriving at the registration zone at the top face. Fig. 4 indicates that the process took about 5 ms assuming that a non-flat combustion front was sufficiently flat for a given time resolution.

The analysis of the data showed that the main chemical transformations occurred during 70–80 ms. Taking into consideration the results above, the reaction process can be divided into stages.

In the first stage (0–20 ms) the combustion front approached the registration zone and heated the Ni and Al particles. The intensity of the Ni peak was decreased, whereas the intensity of the Al peak remained approximately the same (this requires further investigation) and there are no intermetallide or other phase peaks observed. At the same time, no liquid phase formed (diffuse scattering intensity was low).

The second stage took place during the next 20–45 ms. It was accompanied by a further decrease of the Ni peak, a decrease of the Al peak and the appearance of a new intermetallide peak. Simultaneously a melting process occurred (an increase of the diffuse scattering intensity was observed). The Al peak disappeared at the end of this stage. We assume that the Al melted and liquid Al interacted with Ni particles, giving NiAl.

The next stage persisted 70–80 ms from the start of the reaction. The Ni particles continued to react with melted Al until they were completely consumed by the reaction.

During the final stage (80 ms–70 s) the Debye ring of the intermetallide was divided into separated spots (see Fig. 2). The intensity

of the spots was increasing, suggesting a recrystallization process. We would like to note that spots from the crystallites were slightly disordered owing to imperfections in the crystallites *etc.* If we had used a one-coordinate detector we should have obtained two closely spaced peaks. Many researchers have interpreted these peaks as new phases, whereas there was only one phase in our opinion.

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