



In situ observation of self-propagating high temperature syntheses of Ta₅Si₃, Ti₅Si₃ and TiB₂ by proton and X-ray radiography



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ABSTRACT

Self-propagating high temperature reactions of tantalum and titanium with silicon and titanium with boron were studied using proton and X-ray radiography, small-angle neutron scattering, neutron time-of-flight, X-ray and neutron diffraction, dilatometry and video recording. We show that radiography allows the observation of the propagation of the flame front in all investigated systems and the determination of the widths of the burning zones. X-ray and neutron diffraction showed that the reaction products consisted of ≈ 90 wt% of the main phase and one or two secondary phases. For the reaction $5\text{Ti} + 3\text{Si} \rightarrow \text{Ti}_5\text{Si}_3$ flame front velocities of 7.1(3)–34.2(4) mm/s were determined depending on the concentration of a retardant added to the starting material, the geometry and the green density of the samples. The flame front width was determined to be 1.17(4)–1.82(8) mm and depends exponentially on the flame front velocity. Similarly, for the reaction $\text{Ti} + 2\text{B} \rightarrow \text{TiB}_2$ flame front velocities of 15(2)–26.6(4) mm/s were determined, while for a $5\text{Ta} + 3\text{Si} \rightarrow \text{Ta}_5\text{Si}_3$ reaction the flame front velocity was 7.05(4) mm/s. The micro structure of the product phase Ta₅Si₃ shows no texture. From SANS measurements the dependence of the specific surface of the product phase on the particle sizes of the starting materials was studied.

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1. Introduction

Self-propagating high temperature syntheses (SHS) or combustion syntheses are well established techniques to exploit strongly exothermic reactions for the synthesis of ceramics. In a typical experiment, the reaction is started in a sample made from a compacted powder mixture of the starting materials by a local ignition. The initial reaction releases a large amount of heat and subsequently a combustion wave travels through the sample. As the heat released is sufficient to maintain the combustion wave, this approach has been called self-heating (or self-propagating) high-temperature synthesis. The combustion wave velocity during these reactions is in the range of 1–20 mm/s [1].

Combustion synthesis reactions in which the lowest eutectic temperature in the system is higher than the reaction temperature are often called solid flame reactions, as under these constraints

there are no liquid or gaseous components present [2]. In such a solid–solid reaction the sample may retain its shape, and hence solid flame reactions offer the possibility of a “near-net-shape” synthesis of refractory compounds [3]. This is of interest especially for the synthesis of ultrahigh temperature ceramics, which are difficult to machine [4].

Numerous compounds have been prepared by SHS, including metal oxides, carbides, silicides and borides [1,5,6]. However, in order to fully exploit the potential of this synthesis route for the energy efficient synthesis of materials relevant to scientific and industrial applications, a knowledge of the kinetics of these reactions is essential. Earlier studies have already demonstrated that reaction parameters such as the flame front velocity or the activation energy strongly depend on the shape and dimensions of the specimen, the particle size and the density of the compacted starting materials (“green density”). Numerous studies have addressed the propagation of the reaction front in solid-flame reactions by e.g. optical and pyrometric techniques limited to the surface [7,8,5]. However, all the techniques employed up to now are limited to the observation of processes on or close to the surface, as the penetration depth of X-rays is a

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few hundred μm for typical transition metal compacts and the thermal emission originates essentially from the surface only. Here we propose to use alternative observational techniques, based on transmission measurements. We show that both hard X-ray and proton radiography are well suited to measure the flame front velocity and the width of the flame front. We compare the radiography results complement these experiments by X-ray and neutron diffraction measurements, video recordings and dilatometry.

2. Experimental

2.1. Sample preparation

The starting materials were mixed in a stoichiometric ratio, ground for approximately 15–20 min and pressed into pellets. The powders which were used had a particle size of -325 mesh ($<44 \mu\text{m}$), except for boron where no particle size information was available. Tantalum was also used with a particle size of $2 \mu\text{m}$. The purity of the samples was 99.9% for tantalum (Alfa Aesar), 99.999% for silicon (Alfa Aesar), 95–97% for amorphous boron (Sigma–Aldrich) and 99% for titanium (Strem Chemicals). The pellets were mostly cylindrical samples with a diameter of 6 mm and a height of 15 mm (Table 1). In addition, we pressed larger cylindrical samples with a diameter of 10 mm and a height of 7 mm, and rectangular samples with dimensions $5.0 \times 6.0 \times 8.4 \text{ mm}^3$ and $5.0 \times 10.0 \times 9.7 \text{ mm}^3$. In order to slow down some of the reactions, an inert material was added as a retardant [2]. In all cases this inert material was the correspondent product phase.

2.2. X-ray radiography

X-ray radiography was performed with the bremsstrahlung spectrum of two tungsten anodes, arranged at 90° to each other and an acceleration voltage of 100 kV. Two detectors (one CCD from Photometrics with a time resolution of 10 frames per second and a CMOS-based Vision Research Phantom camera with 300 frames/s) were employed. The spatial resolution quoted by the manufacturers is $\approx 100 \mu\text{m}$. For the present experiments, the samples were contained in a reaction container which was continuously purged with argon. Ignition was achieved by resistively heating a tungsten coil placed close to the top of the samples.

2.3. Proton radiography

The proton radiography was performed using 800 MeV protons from the LANSCE accelerator. The experimental set-up is described in more detail in Ref. [9]. For the present experiments, a time resolution of 10 frames per second and a nominal spatial resolution of $\approx 100 \mu\text{m}$ was chosen. The samples were placed into sample containers which were continuously purged with helium at ambient pressure. Ignition was achieved by resistively heating a tungsten coil placed close to the top of the samples. The cuboid samples were placed in the chamber so that the proton beam was perpendicular to the largest face.

2.4. Video recording

Videos were recorded with a temporal resolution of 30 frames/s and 1280×720 resolution, using a video camera (Toshiba, Camileo SX500). The experiments were performed in a reaction chamber in an argon atmosphere.

2.5. Dilatometry

Thermal expansion was measured with a commercial push-rod dilatometer (Netzsch DIL 402C) equipped with an inductive displacement transducer. Samples were measured at temperatures between 473 K and 93 K in a Netzsch cryofurnace. Each sample was measured at least three times with heating and cooling rates of $\pm 1 \text{ K/min}$. During the measurement, the sample environment was flushed with dried helium gas.

2.6. Small-angle neutron scattering

Small-angle neutron scattering (SANS) using LQD at LANL [10,11] was employed to study the scattered intensity of thin sample slices for scattering vectors of $Q = 0.004\text{--}0.1 \text{ \AA}^{-1}$. The samples were measured for $\approx 2 \text{ h}$. After a background correction the data were normalized by a calibration factor and the thickness of the samples. A power-law fit to the scattering data was then used to obtain the internal surface area.

2.7. X-ray powder diffraction

Phase composition was determined using X-ray powder diffraction with a Panalytical X'Pert Pro diffractometer with a Ge(111) Johansson monochromator, employing $\text{Cu-K}\alpha_1$ radiation. The samples were measured for 16 h from 2° to 100° in 2θ .

2.8. Neutron diffraction

Neutron diffraction to study the phase composition and texture of the product phase has been carried out using the HIPPO (High Pressure Preferred Orientation) time-of-flight diffractometer at LANSCE. This instrument has been described in more detail in Ref. [12]. The samples were measured for an hour and the data were collected from the detector banks at 40° , 60° , 90° , 120° and 145° in 2θ with sample rotations of 0° , 67.5° and 90° counted for 20 min each, resulting in a total count time of 60 min per sample.

3. Results

3.1. Sample characterization

3.1.1. X-ray and neutron powder diffraction

The X-ray and neutron diffraction data were analyzed using GSAS [13] and gslanguage [14]. For the refinement of the neutron diffraction data the banks at 145° and 90° in 2θ were used. The desired main phases constituted $\approx 90\%$ of the samples (Table 2).

The secondary phases observed in the synthesis aimed at producing tetragonal Ta_5Si_3 (ICSD: 108742) [15] are hexagonal Ta_5Si_3 (ICSD: 652324) [16], Ta_2Si (ICSD: 42526) [17] and TaSi_2 (ICSD: 86810) [18]. The synthesis of Ti_5Si_3 (ICSD: 168415) [19] additionally yields small amounts of Ti_5Si_4 (ICSD: 43080) [20]. The reaction of boron with titanium leads to $\approx 97\%$ TiB_2 (ICSD: 659126) [21] and minor amounts of TiB (ICSD: 615596) [22]. Figs. 1–4 show the results of these refinements. The refinement of the TiB_2 (sample no. 47) leads to a higher R_{wp} value in comparison to the other samples due to lower counting rates. On the other hand, the low reduced χ^2 value as well as the smooth difference curve shows that the refinement was successful.

3.1.2. Texture analysis

The texture analysis was performed using the program MAUD [24]. The pole figures were of several crystallographic planes obtained from a refinement of the orientation distribution function using the E-WIMV option, which is based on the Williams–Imhof-

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