Exothermic Self-Sustained Waves with Amorphous Nickel

Khachatur V. Manukyan,*† Christopher E. Shuck,‡ Mathew J. Cherukara,‖ Sergei Rouvimov,§ Dmitry Y. Kovalev,⊥ Alejandro Strachan,∥ and Alexander S. Mukasyan‡,#

†Departments of Physics, ‡Chemical & Biomolecular Engineering, and ‖Electrical Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States
‖School of Mechanical Engineering and School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907, United States
⊥Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia
§National University of Science and Technology, ”MISIS”, Moscow 119049, Russia

Abstract: The synthesis of amorphous Ni (a-Ni) using a liquid-phase chemical reduction approach is reported. Detailed structural analysis indicates that this method allows for efficient fabrication of high surface area (210 m²/g) amorphous Ni nanopowder with low impurity content. We investigated the self-propagating exothermic waves associated with crystallization of Ni from the amorphous precursor. Time-resolved X-ray diffraction indicates that amorphous nickel crystallizes in the temperature range 445−480 K. High-speed infrared imaging reveals that local preheating of compressed a-Ni nanopowder triggers a self-sustaining crystallization wave that propagates with velocity ∼0.3 mm/s. The maximum temperature of crystallization wave depends on the sample density and can be as high as 600 K. The Kissinger approach is used to determine the apparent activation energy (55.4 ± 4 kJ/mol) of crystallization. The self-diffusion activation energy of Ni atoms in a-Ni is ∼60 kJ/mol, determined through molecular dynamics (MD) simulations. This agreement of experimentally derived and theoretically calculated activation energies allows us to conclude that self-diffusion of Ni atoms is the rate-limiting stage for crystallization. Furthermore, utilization of amorphous metal as a reactant significantly increases the rate of solid-state reactions. For example, in reactive intermetallic forming systems, such as Ni + Al, the self-sustaining reaction propagation velocity with a-Ni is twice higher than with crystalline Ni of the same morphology. Additionally, using a-Ni increases the maximum reaction temperature in the Ni + Al system by 300 K.

1. INTRODUCTION

Amorphous metallic materials, usually alloys, are solids that lack long-range order in their atomic-scale structure.1−7 Amorphous metals have unique magnetic,8−11 optical,12,13 and mechanical14−19 properties. These materials can be integrated into magnetic14 and data-storage12 devices. They are also used for a variety of biomedical20−29 and chemical30−39 applications. The conventional methods for preparation of amorphous alloys include rapid solidification,30,31 ion irradiation,32−34 mechanical alloying35−38 and chemical reduction.24−26,39 Characteristics such as number of the components, atomic size mismatch, heats of mixing for the constituent elements, and cohesion between the metals play key roles in the formation of amorphous metallic materials.30,34 Preparation of pure amorphous metals is more difficult than amorphous alloys due to the ease of crystallization. Ultrasonic processing of metal carbonyl or nitrate solutions under an inert atmosphere is a proven approach for production of amorphous metal (Fe, Ni, Ag) nanoparticles with irregular shapes and broad size distributions.40−43 Sonochemically derived amorphous metals have relatively low air stability and require additional protective coatings; typically organic molecules are utilized for stabilization.44,45 Aqueous chemical reduction of transition metal salts by alkali metal borohydrides (NaBH₄ or KBH₄) is also widely used for production of amorphous metals,46−50 but this often instead produces amorphous boron-containing alloys.50 Here, we report a novel method for fabrication of high purity amorphous metal.

The crystallization of amorphous metals and alloys is of interest for a variety of applications.31 Amorphous metals are thermodynamically unstable and under certain conditions can transform into more stable crystalline states.51 Amorphous...
solids may crystallize into polycrystalline phases upon heating, laser impulse, or mechanical deformation. In general, crystallization of solids is categorized into several groups: (i) from solution, (ii) from melt, and (iii) from an amorphous solid. Crystallization from solution is a slow process, evidenced by mineral formation over geological time scales. Crystallizations from melt and amorphous solids are relatively rapid processes. Several distinctive crystallization scales. Crystallizations from melt and amorphous solids are known. Surface-assisted crystallization typically takes place in organic and glassy alloys. Self-propagating crystallization, also termed explosive crystallization, has been observed in thin amorphous silicon films and occurs with velocity up to 50 m/s.

We hypothesize that pure amorphous metals would crystallize in a self-sustaining manner due to the large heat of crystallization and thermal conductivity. Furthermore, we also suggest that utilizing amorphous metals as reactants may significantly increase the rate of solid-state reactions, for example, in intermetallic forming systems. This hypothesis was supported by molecular dynamics (MD) simulations in amorphous Al/Ni nanocomposites.

In this work, we report on the synthesis of high-surface-area amorphous Ni (a-Ni) with low level of impurities using a liquid-phase chemical reduction approach. We also investigated the rapid, self-propagating exothermic process associated with the crystallization of Ni from the amorphous precursor and self-sustained reaction in the Ni + Al reactive system. Large-scale MD simulations provide insight into the kinetics and mechanism of nickel crystallization as well as the role of the nanostructure on the self-propagating crystallization wave.

2. EXPERIMENTAL AND THEORETICAL SECTION

2.1. Material Fabrication. Synthesis of a-Ni is performed by a modification of the liquid-phase reduction approach, which involves nickel nitrate and NaBH₄ as the reducing agent. Pure ethyl alcohol (Coptec, 200 proof) was added to a three-neck flask and cooled using an ice bath to 274 K, and then 2.5 g of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Alfa Aesar) was dissolved in the ethyl alcohol. Nitrogen (Airgas, 99.9998%) was bubbled (100 cm³/min) through the solution for 30 min. Then, 2.0 g of sodium borohydride (NaBH₄, MP Biomedicals, 99%) was dissolved in cold (274 K) water and added to the nickel nitrate solution under vigorous stirring and nitrogen flow. The reaction was allowed to proceed for 30 min, and then the a-Ni precipitate was filtered and washed with deionized water and ethyl alcohol. The purified a-Ni powder was vacuum-dried at room temperature.

2.2. Material Characterization. Crystallinity of the fabricated nickel powder was determined by X-ray diffraction (XRD) analysis with Ni-filtered Cu Kα radiation (D8 Advance, Bruker) operated at 40 kV and 40 mA with step scan of 0.02° and counting time of 20 s in the range of diffraction angle (2θ) 25°–85°. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a PHI VersaProbe II spectrometer with an Al Kα X-ray source operating at 1486.6 eV and a 90° takeoff angle for near surface analysis of Ni 2p and B 1s electronic transitions. The powders were adhered to stainless steel mounts and loaded into the analysis chamber. Samples were outgassed in the vacuum system to a pressure less than ~10⁻⁷ Pa. Argon plasma sputtering for 60 s was used to clean the surface layer of the samples. Binding energy values were referenced to the C 1s peak (284.8 eV) that resulted from the adventitious contamination layer. The spectra were analyzed using the Multipak XPS software package.

A Cameca SX-50 electron probe microanalysis (EPMA) was used for chemical composition analysis to determine the boron quantity in a-Ni. The operating conditions were 15 kV and 100 nA, with the incident electron beam defocused to ~10 μm. The baseline and window of the pulse height analysis was set based on the B Kα peak in order to reduce background and any high-order interferences. Inductive coupled plasma (ICP) analysis was also used to determine the boron content in a-Ni.

Microstructural analysis was conducted in a field-emission SEM Magellan 400 (FEI). A Titan 300 TEM (FEI) with 0.1 nm information limit in high resolution TEM mode was used to analyze the atomic structure of the metals. The Titan is equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford Inc.) system with a spectral energy resolution of 130 eV.

The specific surface area and pore size distribution of the nickel powders were measured by an ASAP 2020 instrument (Micromeritics). Prior to this analysis, the samples were vacuum degassed at 333 K for 15 h. The Brunauer–Emmet–Teller (BET) equation was used to calculate specific surface area. Pore size distributions and pore volumes were determined by Barrett–Joiner–Halenda methods.

2.3. Crystallization Characteristics. A differential scanning calorimeter (Mettler-Toledo) was used to measure the heat of crystallization and kinetics of heat release. In these experiments, 0.05 g of a-Ni was heated to 800 K at heating rates of 70, 85, 100, and 120 K/min in an atmosphere of 99.9998% pure argon with a flow rate of 100 cm³/min.

Time-resolved XRD (TRXRD) was used for in situ monitoring of the crystallization dynamics. The experimental procedure for TRXRD studies can be found elsewhere. Briefly, a compact a-Ni pellet with thickness of 0.2 mm was placed into a reaction chamber and purged with helium (99.9995% pure) prior to uniform heating of the entire sample to ~500 K. The TRXRD system, including a Cu Kα X-ray source, monochromator, and a linear position-sensitive detector, is used to obtain a wide range (2θ up to 40°–80°) of diffraction spectra with a time resolution of 1 scan per second.

The temperature–time history of the self-propagating crystallization was recorded by a 100 μm K-type thermocouple inserted inside pressurized cylindrical samples with 5 mm diameter and relative theoretical maximum density in the range 0.17–0.23. The output signal of the thermocouple is transformed to data storage by a data acquisition system (Data Translation Inc.) and recorded with a 1 kHz frequency using Quick DAC software.

A high-speed infrared (IR) camera (FLIR Systems, SC6000) was used to monitor both the self-propagating crystallization and the exothermic reaction of a-Ni with nanosize Al (ALEX, average particle size 80 nm). The IR camera provides in situ two-dimensional maps for the temperature–time history of the process. The thermal videos were captured over several different temperature ranges, which include temperatures as high as 2200 K and frame rates upward of 20 000 frames/s with spatial resolution of ~5 μm. The velocity of the front propagation was calculated using frame-by-frame analysis of thermal videos.

2.4. Nonequilibrium Molecular Dynamics Simulations. To gain an understanding of the underlying physics of the process of crystallization at the atomic level, we use MD
simulations to study the crystallization velocities and diffusivities of Ni in a-Ni at different temperatures. We studied crystallization in bulk samples as well as samples consisting of nanoscale particles designed to resemble the experimental morphologies. The bulk a-Ni was created from a single crystal of Ni $10 \times 10 \times 45$ unit cells in size. The single crystal, with periodic conditions in all directions, was thermalized at 300 K for 100 ps at 0.1 MPa and heated up to 3000 K in 1000 ps. We use isothermal and isobaric MD simulations (NPT ensemble) in a Nosé–Hoover thermostat and barostat with relaxation time scales of 0.1 and 1 ps, respectively. The molten structure was equilibrated at 3000 K for 100 ps before being cooled down to 300 K in 100 ps, again using the NPT ensemble. To simulate the crystallization process at a given temperature, this amorphous sample was placed in contact with a crystalline seed at one end as shown in Figure 1a. An energy minimization was first performed on the combined structure, before switching to the NPT ensemble at the desired temperature and 0.1 MPa to study the crystallization velocity at the target temperature.

To study the nature of the self-sustaining crystallization wave in the loose amorphous powder, we performed MD simulations of an idealized microstructure representing a chain of a-Ni nanoparticles along which the crystallization front is expected to propagate. Two initially crystalline spheres of Ni of diameters 20 and 10 nm were melted by heating to 2300 K in steps of 25 K, thermalizing for 50 ps at each step using the isothermal MD. This is followed by thermalization at 2300 K for 100 ps, before cooling to 300 K in 200 ps. Finally, these amorphous spheres were thermalized at 300 K for 20 ps, still

---

Figure 1. Initial structures used in the molecular dynamics simulations for (a) crystallization in an assembly of granular particles and (b) crystallization studies in the bulk. Crystalline seed is shown in blue, and amorphous atoms are shown in pink.

Figure 2. Results of electron microscopy imaging of a-Ni: SEM image (a), bright-field TEM image with SAD pattern inset of porous agglomerates (b), and high-resolution TEM images of a-Ni particles (c, d).
under NVT conditions. Eight nanoparticles were then packed in the configuration shown in Figure 1b, with a crystalline seed placed in contact at one end of the ensemble. Following an energy minimization, the entire structure was then thermalized for a further 100 ps at 300 K. To initiate the crystallization wave, a crystalline seed was heated up to 800 K in 20 ps and was then held at that temperature for 100 ps, keeping the rest of the sample under constant energy conditions. Subsequently, the entire sample was switched to the adiabatic conditions (constant energy or microcanonical ensemble).

All simulations were performed using the LAMMPS package, and the equations of motion were integrated with a time-step of 0.5 fs for all simulations. We used the Purja and Mishin EAM potential which was built using a pre-existing Ni potential parametrized by Mishin. This potential reproduces the lattice parameter, melting temperature, elastic constants, and the vacancy and migration energies in Ni and has been used extensively under conditions of elevated temperature and pressure.

3. RESULTS

3.1. Structural Characterization of Amorphous Ni Powder. SEM and TEM images of the synthesized powder are shown in Figure 2. It can be seen that the nanoparticle agglomerates have a size of ~1 μm (Figure 2a). The low-magnification TEM bright field image shown in Figure 2b indicates that the size of these nanoparticles is in the range 10–20 nm. The selected area electron diffraction (SAD) pattern (inset in Figure 2b) and high-resolution TEM image (Figure 2c) reveal that the particles are amorphous. Detailed TEM analysis (Figures 2d,e) indicates that the particles consist of an amorphous Ni core with thin (≥1 nm) shell of crystalline NiO (Figure 2e) that prevents the metal core from further oxidation.

XRD observations (Figure 3) agree well with the TEM analysis. A big hump between 38° and 55° may be assigned to the scattered X-rays from the amorphous nickel, while two broad peaks observed at 34.5° and 60.08° (2θ) may be related to the NiO phase. The results of the XPS analysis (Figure 4) confirm that the surface of the amorphous Ni nanoparticles is oxidized, showing the Ni(II) peak at 855.45 eV, while the sample spectra, after argon sputtering, indicate only the intense metallic nickel peak at 852.8 eV (Figure 4a). XPS analysis also suggests that boron is the major impurity of the as-synthesized amorphous nickel powder (Figure 4b). EPMA analysis reveals that boron quantity in a-Ni is less than 1.5 wt %. Inductively coupled plasma tests also show on overall low B concentration (~1.1 wt %) in the produced amorphous nickel.

Gas adsorption/desorption analysis for the a-Ni powder is presented in Supporting Information Figure 1. The nitrogen adsorption–desorption isotherms of as-synthesized a-Ni powder exhibit a narrow hysteresis loop, indicating the presence of both micropores (pores size <2 nm) and mesopores. The size distribution of mesopores reveals a large portion of pores with diameters in the range 2–9 nm. The specific surface area of a-Ni powder calculated from linear range of adsorption isotherm using BET method is 210 m²/g.

Thus, the developed chemical reduction method allows the efficient fabrication of high surface area amorphous Ni nanopowder with a thin NiO passivating layer and relatively low boron impurity.

3.2. Exothermic Self-Propagating Waves. We investigated the kinetics of amorphous Ni crystallization using DSC at different heating rates (β = 70, 85, 100, and 120 K/min). Figure 5a demonstrates that at β = 70 K/min the onset temperature of crystallization (T_o) and temperature of maximum heat release (T_m) are 422 and 458 K, respectively. The net heat released during the crystallization is measured to be ~0.16 kJ/g. An increase in the heating rate results in a shift of the exothermic peak toward a higher temperature. The Kissinger approach was used to analyze the DSC data at different heating rates for determining the apparent activation energy of crystallization. Figure 5b shows a Kissinger plot of the DSC data that results in an activation energy of 55.4 ± 4 kJ/mol.

We also utilized in situ TRXRD to study the crystallization kinetics during external heating conditions (Figure 6). The results (Figure 6a) show that at β = 120 K/min long-range order starts to develop at a temperature of 445 K, which is in good agreement with DSC data. Figures 6b,c show several XRD patterns acquired at different stages of crystallization and kinetics of intensity for the Ni (111) diffraction peak. These results show that crystallization completes at 480 K, which corresponds to T_m determined by DSC. The results of DSC and TRXRD analysis suggest that the exothermic crystallization of a-Ni takes place between ~420 and 480 K during external heating conditions, with characteristic time scale on the order of few seconds.

In order to explore self-propagating crystallization, cylindrical samples of a-Ni with 5 mm diameter and 15 mm height were compacted to different relative densities. The samples were...
placed into a reactor, which was first outgassed to a pressure of \( \sim 10^{-3} \) Pa and then filled with argon gas to 0.5 MPa. A resistively heated tungsten coil was placed on the upper surface of the sample, which was locally preheated to 500 K and the heater was turned off 2 s after. High-speed infrared imaging showed that after such local preheating the self-sustained crystallization wave propagates along the sample. Figure S2 demonstrates several snapshots of high-speed infrared imaging video of the propagating crystallization wave.

The crystallization wave propagation velocity was investigated using frame-by-frame analysis of the infrared video and by plotting the position vs time for samples with different relative densities (Figure 7a). It can be seen that the front propagates relatively steadily for the sample with 0.17 TMD, while some local fluctuations in the velocities can be seen in more dense samples (e.g., 0.23 TMD). The average wave propagation velocity varies in the range 0.25–0.4 mm/s. Typical temperature–time profiles measured by a microthermocouple for the sample with 0.19 and 0.23 TMD are shown in Figure 7b. The maximum temperature of self-propagation crystallization depends on the sample density and ranges from 460 to 600 K.

XRD analysis shows that the self-crystallized Ni (c-Ni) samples possess all diffraction peaks of face-centered-cubic (FCC) nickel (Figure 3b). Detailed analysis reveals that the peak deviation, compared to the standard FCC nickel phase diffraction data (JCPDS 65-2865), is only 0.07%. TEM observations show that the size of agglomerates after self-propagating crystallization is on the same order as a-Ni (Figure 8a). The SAD pattern and high-resolution TEM images show that those agglomerates are crystalline (Figure 8b–d). High-resolution TEM images in Figure 8c,d suggest that aggregates of c-Ni are polycrystalline and the interplanar spacing of the (111) plane of the nanocrystals is \( \sim 0.2040 \) nm. It should be noted that the interplanar spacing for the same plane in FCC nickel is 0.2035 nm.
We also explored the differences in combustion front propagation in the Ni + Al reactive system. In these experiments, a-Ni and Al nanopowders in a 1:1 molar ratio were thoroughly mixed to ensure a uniform distribution of the nanoparticles (Figure S3). The as-prepared mixture was compacted to a relative density of 0.65 into cylindrical samples (5 mm diameter, 15 mm height). In order to understand the effect of a disordered structure on the combustion characteristics of reactive mixtures, some a-Ni samples were inserted into a quartz tube and were slowly heated to 450 K in flowing argon to crystallize nickel (c-Ni). The prepared samples, one with a-Ni and one with c-Ni, were inserted into a stainless steel chamber with infrared transparent sapphire windows, where self-propagating reaction was initiated by local heating of the samples in an inert gas atmosphere. High-speed infrared imaging indicated that the front propagation velocity for the a-Ni + Al sample (12 mm/s) is almost twice larger than that of the c-Ni + Al case (7 mm/s). Also, a significant difference in combustion temperatures was observed. The a-Ni + n-Al sample exhibited a maximum combustion temperature of 2100 K, while the c-Ni + n-Al sample is only 1800 K (Figure 7c). The microstructures of the combustion products also show significant differences (Figure S4).

To better understand the experimentally observed results, we used molecular dynamics to study the underlying physics behind the self-propagating crystallization wave in a-Ni.

3.3. Molecular Dynamics Simulations. 3.3.1. Crystallization Kinetics in the Bulk. We first consider the crystallization in bulk a-Ni, using the simulation setup described in section 2.4. A crystalline seed is placed in contact with the amorphous samples, and the crystallization velocities are calculated at different temperatures. Snapshots of the simulations at $T = 1200$ K are shown in Figure 9. Figure 10a demonstrates the crystallization velocities as a function of temperature. The simulations reveal the expected temperature behavior. At low temperatures the crystallization wave velocity increases with increasing temperature as atoms become more mobile. Beyond a certain temperature, however, the crystallization velocity slows as the driving force for crystallization (difference in free energy between the two phases) decreases and eventually becomes zero when the free energies of the amorphous and crystalline phases become equal. Experimental measurements of crystallization from the amorphous phase in bulk Ni are not available; thus, direct comparisons are not possible. Yet, the velocities calculated from MD simulations are similar to the experimental values reported for the crystallization of silicon.84 Interestingly, these values are orders higher than those observed experimentally for the porous samples studied here.
tends to zero and the velocity expression is reduced to a single exponential. The calculated activation energy of the MD simulations is $\sim 5$ kJ/mol (fit shown in Figure 10b). This number is significantly smaller than that as the experimentally derived activation energy ($55.4 \pm 4$ kJ/mol).

To better understand the physical origin of this low activation energy, we compare this value to the activation energy of self-diffusion of a-Ni in amorphous Ni. Figures 11a,b show the average mean-square displacements (MSD) of Ni atoms in the bulk a-Ni sample at 1200 and 1400 K. The diffusion constant is given by the slope of the linear fit to the squared displacements as shown by the thin green lines. Figure 11c shows the extracted diffusion coefficients on an Arrhenius plot. The calculated activation energy for the self-diffusion of Ni atoms in a-Ni is found to be $\sim 60$ kJ/mol, which is very close to the above-reported experimentally derived activation energy of a-Ni crystallization. These results suggest that diffusion is the kinetic governing process in the DSC crystallization experiments.

### 3.3.2. Crystallization Dynamics in the Amorphous Powder

As mentioned in the previous section, the calculated crystallization velocities in bulk a-Ni are considerably higher than the experimentally observed values. To simulate the crystallization wave in the amorphous powder, we consider the propagation of the crystallization wave in a single, connected chain of amorphous nanoparticles. As described in section 2.4, a crystalline seed that is held at 800 K for a short duration is placed in contact with one end of this amorphous chain. Figure 1b shows the initial configuration. Subsequently, the thermostat on the crystalline seed is switched off and the entire simulation is run under constant energy conditions (NVE ensemble). A self-propagating crystallization wave initiates and propagates along the length of the amorphous particle assembly. Figure 12a shows the fraction of the crystalline material in the sample over time. Also, atomic snapshots from the simulation at different times are presented in Figures 12c–f. FCC atoms are indicated in green, and atoms in the amorphous Ni are translucent orange. Red atoms denote stacking faults (HCP atoms) in the FCC that develop in the crystalline material during growth. It can be seen initially that the transformation rate is quite slow as a consequence of the small contact area between the hot seed and the amorphous material, which is at 300 K ($<1.5$ ns). Growth during this early stage is also inhibited by the divergent flow of heat away from the crystallization front within the particle. Figure 12b reveals the average local temperatures as a function of position along the amorphous particle chain. During the initial stage ($<1.5$ ns), the temperature within the particle is essentially uniform, with a sharp drop in temperature to the next particle due to the poor contact between them. During the next stage of the transformation (2–3 ns), a sharp increase in the velocity of the crystallization front occurs.

During this time-period, half of the first particle is transformed and the process is aided by the poor thermal transport between particles. The heat conduction away from the crystallization front becomes convergent. The temperature within the first particle also reaches its highest value at this point (see Figure 12b). Once the first particle has completely transformed, an immediate drop in the transformation rate takes place, as the crystallization front begins to advance into the second particle. This decrease in rate is due to divergent heat flow away from the point of contact and the lower temperature in the second particle. Similarly, once half the
second particle has crystallized, a sharp jump in transformation velocity is observed. This stuttering growth of the crystalline front repeats multiple times as the crystallization front traverses the amorphous chain. The MD simulation described above shows the importance of particle–particle contacts in limiting the crystallization rate. Poor thermal contact between particles dramatically slows the crystallization front and prevents the wave from attaining steady state. As a result, the estimated crystallization velocities (~6 m/s) are almost an order of magnitude lower than the calculated velocities in the bulk. The simulations described above represent an idealization of a segment of the amorphous powder. The actual microstructure is far more disordered (Figure 2) and has less density (~20%), which is half of the packing density (~40%) used in the MD simulation. Furthermore, we do not account for the presence of an oxide layer on the a-Ni particles, which should lead to further reduction of the thermal transport at particle contacts, as well as act as a barrier to the crystallization wave. Indeed, in this case, the crystallization may require independent nucleation within each particle.

Figure 11. Average mean-square displacement (MSD) vs time of Ni atoms in amorphous Ni at 1200 K (a) and 1400 K (b) and Arrhenius plot of extracted diffusion coefficients (c).

Figure 12. Crystallized fraction vs time for the amorphous particle assembly (a); averaged local temperatures vs position for the times (b) marked out in (a). Snapshots of the recrystallization wave at 1 (c), 3 (d), 5 (e), and 8 ns (f). FCC atoms are in green, HCP atoms are in red, and atoms in the amorphous are in translucent orange.
4. DISCUSSION

This work has led to several discoveries for amorphous metals: (i) amorphous nickel with low level of boron impurity, high specific surface area, and particle size less than 20 nm was synthesized by chemical reduction using sodium borohydride; (ii) for the first time it was demonstrated that crystallization of a-Ni may occur in self-sustaining mode; (iii) reaction parameters and products in intermetallic forming systems (e.g., Ni + Al) can be tailored by use of amorphous metal reactants.

We have developed a synthesis formulation for liquid-phase reduction of metals using KBH₄ or NaBH₄ and applied ethanol solution of nickel nitrate as a reagent. Previous work has focused on the aqueous-phase reduction of nickel chloride or acetate. Furthermore, in conventional recipes the reducer solution is usually added dropwise with constant mixing, while in our case the entire reducer was added instantly to the nickel nitrate solution under vigorous magnetic stirring conditions. Such rapid nonequilibrium conditions apparently influence the morphological characteristics of the solid product and, more importantly, prevent diffusion of boron into the a-Ni structure.

It was previously reported that aqueous-phase reduced Ni contains 5–10 wt % (25–40 at. %) of boron. In this work, boron content in amorphous Ni is below 1.5 wt % (7 at. %). According to the Ni–B phase diagram this composition may correspond to a solid solution of boron in Ni. Additionally, XRD analysis of the self-crystallized product shows only diffraction peaks of pure FCC Ni phase and no peaks of nickel borides (Ni₅B or NiB) or other metastable boride phases. High-resolution TEM analysis also indicates that interplanar spacing of self-crystallized nickel is close to that of pure FCC Ni, thus suggesting that boron impurity has essentially no influence on the crystallization process.

The results of DSC and TRXRD experiments reveal that exothermic crystallization of a-Ni takes place in the range of 420–480 K. The net heat released during the crystallization is ~0.16 kJ/g, which matches the value calculated from MD simulations (~0.16 kJ/g). The apparent activation energy of crystallization determined from a Kissinger analysis of the DSC plots is 55.4 ± 4 kJ/mol, which is close to the activation energy for the self-diffusion of Ni atoms obtained from MD simulations. Agreement of experimentally determined and theoretical data suggests that the self-diffusion of Ni atoms is the rate-limiting stage for the crystallization process.

Significant differences between the experimentally measured velocity (~0.3 mm/s) of self-crystallization and the estimated velocity (~6 m/s) of the simulated process may be attributed to the presence of a NiO layer and extremely high porosity (~80%) of the real powder samples. Both of these effects are not accounted for in the MD model. The porosity and oxide layer both reduce the thermal transport at particle-to-particle contacts and act as a barrier for the crystallization wave. The presence of such barriers should significantly reduce nucleation and growth rates of the crystalline metal phase on the particle-to-particle contacts, and observed frontal crystallization may be considered as a chain of localized events within each particle.

This velocity reduction effect is similar to what is observed for the combustion wave propagation in gasless systems when the chemical reaction rate inside each chemical “cell” exceeds the interparticle heat transport, known as the “relay race” mechanism of reaction propagation. This mechanism explains why the typical velocity of the transformations in the Ni–Al powder mixture is 2 orders of magnitude slower, ~0.01 m/s compared to ~10 m/s, for the same system organized in a form of pore-free, oxygen-free foils.

Finally, usage of a-Ni allows for significantly increased rate of gasless reaction in the Ni–Al system. Our results indicate that the front propagation velocity with crystallized Ni is almost twice lower than the a-Ni + Al sample. The results of our recent work show that an amorphous phase, in this case created by high energy ion irradiation, significantly decreases the thermal ignition temperatures and ignition delay times of Ni/Al reactive multilayer foils. The amorphous interlayer is thought to enhance the reactivity of Ni/Al nanomaterial by increasing the heat of the reaction and by accelerating the interatomic diffusion.

Time–temperature profiles of combustion wave in a-Ni + Al and c-Ni + Al samples (Figure 7c) presented in this work indicate that the maximum combustion temperature of a-Ni + Al sample is 2135 K, while the temperature of c-Ni + Al system is lower by 300 K. It is clear that the exothermic crystallization of a-Ni contributes to the overall thermal regime of reaction and increases the temperature of the process. It is important that the calculated adiabatic combustion temperature in the Ni + Al system is ~1933 K. This means that utilization of amorphous metallic reactants allows us to accomplish “super-adiabatic” processes and significantly increase the overall reaction rate. This experimental result validates the prediction suggested by the MD simulation.

5. CONCLUSIONS

A new synthesis formulation for liquid-phase reduction of nickel nitrate using NaBH₄ was developed for producing amorphous nickel with a low level of impurities. Amorphous nickel exothermically crystallizes at the range of 420–480 K. The apparent activation energy of crystallization was determined to be ~55.4 kJ/mol, which is close to the activation energy for the self-diffusion of Ni atoms obtained from MD simulations. The results indicate that amorphous nickel can be crystallized in a self-sustaining process due to the high heat of crystallization and high thermal conductivity. As a reactant, amorphous nickel significantly increases the rate of gasless reaction in the Ni + Al system. The amorphous reactant is thought to enhance the reactivity of the system by increasing the heat of the reaction and by acceleration the diffusion processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00752.

Results of nitrogen adsorption–desorption analysis of and calculated pore size distribution of a-Ni (Figure S1); snapshots of infrared imaging self-propagating crystallization (Figure S2); SEM images of a-Ni mixture with Al nanopowder (Figure S3); SEM images of NiAl products obtained by combustion of a-Ni + Al and c-Ni + Al samples (Figure S4) (PDF)

AUTHOR INFORMATION

*E-mail kmanukya@nd.edu (K.M.).
Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
Funding was from the Defense Threat Reduction Agency (DTRA), Grant HDTRA1-10-1-0119. Counter-WMD basic research program, Dr. Suhithi M. Peiris, program director, is gratefully acknowledged. This work was also supported by the Department of Energy, National Nuclear Security Administration, under Award DE-NA0002377. This work was also partially supported by the Ministry of Education and Science and Education of the Russian Federation in the framework of Increase Competitiveness Program of NUST “MISIS” Grants K2-2014-001 and K3-2015-016. The authors also thank Sergey Vadhchenko for sample preparation in TRXRD analysis.

REFERENCES


