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The effect of energy deposition on the formation of nanoscale alumina particles in the electrothermal plasma synthesis of nanomaterials

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The electrothermal gun is a relatively new technology that produces various types of plasma vapor using high current pulsed power. A dense metal vapor plasma at extremely high temperature and high velocity is discharged from the electrothermal gun, and introduced into the background gas in the reaction chamber. Then, the discharged metal plasma vapor reacts with background gas and produces nanoscale ceramic particles. Although this method can be applied to make a variety of nanosized ceramic materials by choosing different metals for the cathode/anode/bore ablation and different gases in the reaction chamber, in this investigation, nanoscale alumina particles have been produced by letting a highly ionized aluminum plasma vapor react with oxygen gas in the reaction chamber. The synthesized alumina powder has been characterized by X-ray diffraction, BET, SEM, and TEM. XRD patterns confirmed that low energy firing of 44 kJ energy deposition produced high purity γ-phase alumina nanoparticles, which sizes ranging between 5 and 50 nm with an average particle diameter of 26 nm. By contrast, a high energy shot of 96 kJ produced alumina particles of 41 nm average particle diameter and a small amount of δ- and α-phase contents were found even though γ-phase alumina was still dominant. In addition, high-speed video imaging revealed delayed turbulent mixing and reaction between aluminum plasma vapor and oxygen gas to several milliseconds after approximately 1 ms current pulse duration.

Key words: Electrothermal gun, Metal plasma vapor, Nanoscale alumina powder.

Introduction

Nanoscale ceramic powders, whose particle size is typically below 100 nm, have been attracting many intense scientific and engineering investigations for over a decade, since they provide novel features and significant advantages over conventional powders with larger particle sizes. Among these nanosized ceramic powders, there exists a large industrial demand for ultra-fine alumina (Al_2O_3) for a wide variety of industrial applications including as heterogeneous catalysts, high-performance abrasives, electronic and optical devices, and more, because of its exceptional mechanical, thermal, chemical, optical, and dielectric properties. These nanostructured particles are difficult to produce by conventional mechanical processing. Therefore, numerous processes mostly employing gas to particle conversion have been developed for producing nanosized ceramic particles [1]. Flame synthesis is the most popular approach in producing oxide nanopowders by introducing liquid or gas precursors into the flame environments [2]. Yet another approach gaining popularity is the thermal plasma technique where the precursors are injected into thermal plasma jets produced by a plasma torch [3]. Laser ablation processes employ the metal vapor produced by the laser heating of metal surfaces or micrometer-size powders and reaction of metal vapor with the ambient gases [4], while the exploding wire technique employs the vaporization of metal wires and reaction of metal vapor with the ambient gases [5].

An electrothermal gun is a unique device powered by high-magnitude current pulses to produce various types of pulsed plasma vapors. This device has been originally developed to improve the acceleration of a projectile by the high-pressure and high-velocity plasma jet as an alternative to a conventional propellant igniter [6]. Recently, a new type of electrothermal gun was designed and tested to produce various nanophase ceramic and metallic particles by the reaction of a discharged metal plasma jet with the background quenching gas [7, 8], and those investigations showed that plasma synthesis by an electrothermal gun could be a promising candidate for the energy-efficient production of high quality nanophase materials.

This investigation presents the electrothermal synthesis of nanostructured alumina particles using the redesigned and upgraded electrothermal gun. This process has the potential to be an efficient method for producing novel nanomaterials using a relatively simple setup and can be extended for the production of a wide variety of nanostructured oxides and nitrides as well as nanosized metallic powders.

Experiments

Electrothermal Gun

The electrothermal gun or electrothermal-chemical gun is

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a new high-power pulsed device for producing plasma vapors of various metals such as aluminum and titanium vapors [8, 9], and these metal plasma vapors can be used in the synthesis of novel nanoscale materials. The process employs electrode erosion to vaporize one or both electrodes, and the eroded metal vapor is subsequently ionized to form a dense plasma through which a high current discharge is sustained. The plasma vapor then exits the open end of the bore to create a high-velocity, high-temperature, high-pressure and highly ionized external plasma jet in the controlled background gas in the reaction chamber.

A schematic diagram of the electrothermal gun and the experimental setup is shown in Fig. 1. The electrothermal gun is driven by a pulse-forming network (PFN), which consists of the capacitor bank (C), inductors (L), resistors (R), and the ignition switch. Both the capacitors and the inductors can be varied to apply a wide variety of current, energy, voltage, and pulse duration time. The maximum voltage from the capacitor bank is 11 kV, while the maximum output current is 500 kA. The maximum energy stored in the capacitor bank is approximately 1.2 MJ.

The electrodes are made of aluminum and an aluminum fuse wire is used to initiate the plasma discharge. The bore of the electrothermal gun is 6.65 mm in diameter and 13.5 mm in length and is made of erosion-resistant aluminum oxide. When the ignition switch (S1) is closed, a current discharge is then initiated, and the aluminum electrodes are explosively vaporized. The plasma column inside the bore is subjected to intense Joule heating. The resulting high pressure plasma flow expands rapidly from the open end of the bore into the reaction chamber. Theoretical calculations [9], based upon a quasi-steady, one-dimensional plasma flow model, indicate that the peak velocity and temperature of the plasma flow at the bore exit can reach 6 km/s and 45,000 K, respectively, while the maximum bore plasma pressure is above 100 MPa. At this stage, the aluminum plasma vapor is shown to be completely ionized and plasma consists mostly of Al^{++} ions at the bore exit. The discharged metal plasma vapor will experience extremely rapid expansion and cooling in the reaction chamber and produce nanoscale ceramic particles after mixing and reacting with the background gas.

Gun Operation and Material Characterization

For the present investigation of nanosized alumina synthesis, two different settings of gun operation were employed by varying the initial capacitor charging voltage in the pulse forming network: 3.5 and 5.1 kV, which results in an energy deposition of 44 and 96 kJ, respectively, across the plasma column in the bore. Fig. 2 shows the temporal traces of current and energy deposition during the plasma discharge for the case of the 5.1 kV initial capacitor voltage. The pulse duration was approximately 1.07 ms, while the maximum current was 99 kA at 0.46 ms after the triggering the electrothermal gun. In the lower energy gun firing (44 kJ), maximum current and pulse duration were measured to be 65 kA and 1.05 ms, respectively. In both cases, the plasma vapor was discharged into the quiescent air at atmospheric conditions in the reaction chamber. Additionally, the gun firing at 5.1 kV charging voltage (96 kJ of energy deposition) was tested with a nitrogen environment in the reaction chamber.

During the electrothermal gun operations, sequential images of the visible emission were obtained through the optically accessible 14.5 cm diameter porthole on the side of the chamber, as shown in Fig. 1, using a high-speed video camera system (Redlake Motion Scope HR2000). Temporal evolution of the plasma discharge in the reaction chamber was recorded at the rate of 2000 frames per second, which corresponds to a time resolution of 500 μs. In each frame, the camera exposure

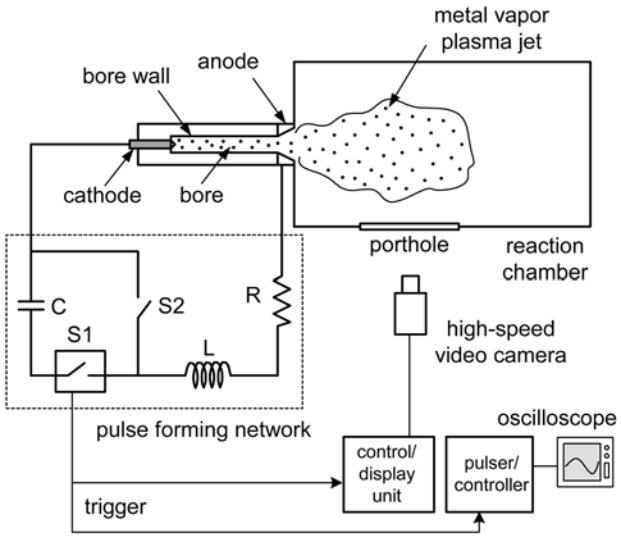

Fig. 1. Schematic diagram of electrothermal gun experimental setup.

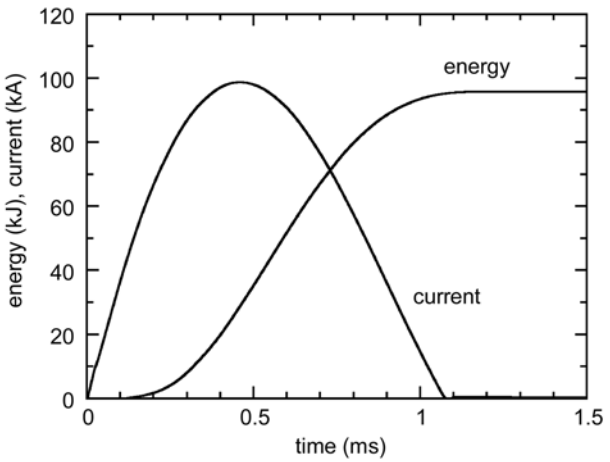

Fig. 2. Measured temporal traces of current and energy deposition during gun operation (initial capacitor charging voltage of 5.09 kV and energy deposition of 96 kJ)

time was 25 μs. Note that the center of the porthole is located at a distance of 34 bore diameters (or 22.7 cm) from the bore exit of the electrothermal gun.

After the electrothermal gun firings, the synthesized nanoparticles were allowed to settle down on the collection plate in the reaction chamber for approximately 12 hours of sedimentation. The material content of the powder samples collected was tested by the X-ray diffractometer (XRD) to identify the crystalline structure of the synthesized material. The particle morphology was investigated using an Hitachi S-4500 field emission scanning electron microscope (SEM) and JEOL 200CX transmission electron microscope (TEM). Also, the Brunner-Emmett-Teller (BET) method was used to measure the specific surface area of the collected powder samples.

Results and Discussion

Electrothermal Gun Operation and Plasma Discharge Evolution

High-speed camera images of the external plasma discharge in the reaction chamber were obtained for the tests fired into the air and the nitrogen gas. Fig. 3 shows the sequential images of the aluminum vapor plasma discharged into the air in the chamber at every millisecond. Additionally, total luminosity of the individual images was evaluated by integrating the relative brightness through time, as shown in Fig. 4. Although the images of the plasma discharge into the nitrogen gas are not shown in this article, the relative brightness was quantified as well and compared with the case of the plasma discharge into the air environment. Keeping in mind that the plasma pulse time scale of the gun is approximately 1 ms and the images were completely saturated during the pulse duration, the camera images may reveal the possible reaction of the aluminum vapor with the oxygen after the evolution of the initial plasma discharge.

While the plasma discharge into nitrogen gas does not show any luminosity after the first few milliseconds of initial plasma firing, the plasma discharge into air environment shows two additional peaks of luminosity. The first peak lasts approximately 3 ms and reaches a maximum at approximately 6 ms after gun triggering, which can be observed also in Fig. 3. This is due to chemical reaction of aluminum plasma vapor with the oxygen content in the air. As studied by Kohel et al. [10] and Kim et al. [11], the temporal plasma discharge from the bore exit creates a strong underexpanded shock structure and a hemispherical contact surface that divides the discharged plasma vapor and background gas. Therefore, turbulent mixing and major reaction between the plasma vapor and the background gas is delayed to approximately 4 ms after the initiation of firing since rigorous mixing occurs after the plasma jet expands enough into the background gas and loses penetrating power. On the other hand, the second peak of luminosity is much weaker than the first one and lasts more than 10 ms. A reasonable explanation is believed to be the reaction of molten aluminum particles of micrometer size with oxygen and this reaction is expected to be much less intense and slower than the reaction of ionized aluminum vapor with oxygen.

The mass erosion from the aluminum cathode was found to be approximately 0.06 g and 0.12 g for low (44 kJ) and high energy firings (96 kJ), respectively, by

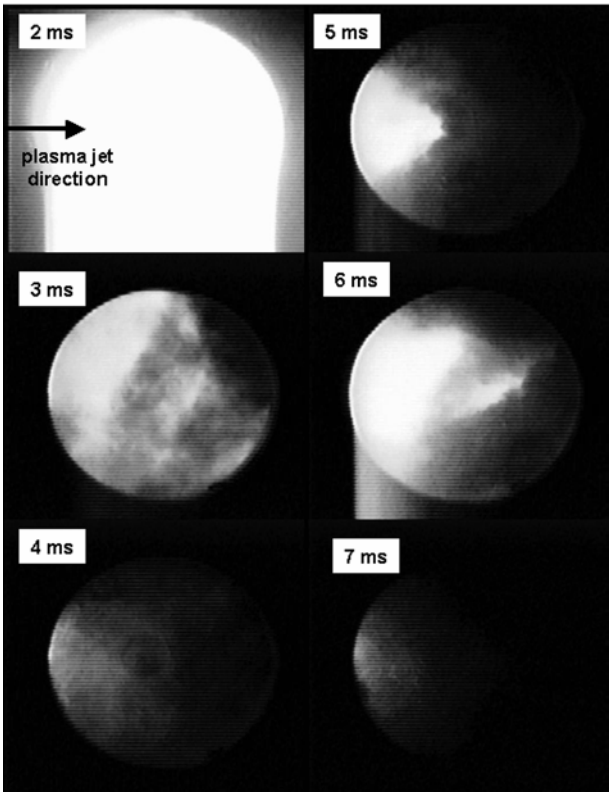

Fig. 3. Sequential high-speed camera images of the plasma jet discharged in an air environment (high energy firing).

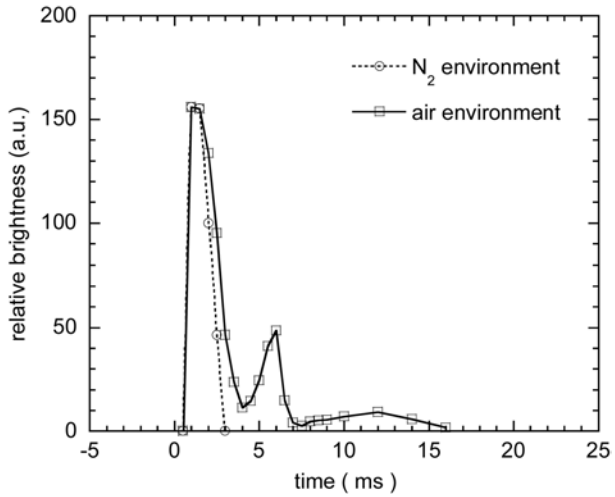

Fig. 4. Relative brightness of the plasma jet fired into reaction chamber filled with air and nitrogen (quantified from the temporal images of high-speed camera photography).

measuring the cathode mass before and after the electrothermal gun firings. As established in other research [7], the electrode erosion subjected to Joule heating is almost linearly proportional to the energy deposition.

Material Characterization of Nanoscale Alumina Produced

To evaluate the average particle size of the samples collected, BET tests were performed and the result shows a specific surface area of 72 m^2/g for low energy firing and 45 m^2/g for high energy firing. By assuming spherical particles, the average particle diameter can be estimated as $\bar{d} = 6/\rho S$ where ρ is the density of the alumina (3.97 g/cm^3) and S is the specific surface area. The estimated average particle diameters based on surface areas are found to be 26 nm and 41 nm for the materials collected from low and high energy firings, respectively. The particle morphology of the particles collected was investigated using SEM and TEM micrographs. Figs. 5 and 6 show the collected alumina nanoparticles produced in the low energy firing into the air environment, where the alumina nanoparticles have a spherical shape with the diameter ranging mostly between 5 and 50 nm.

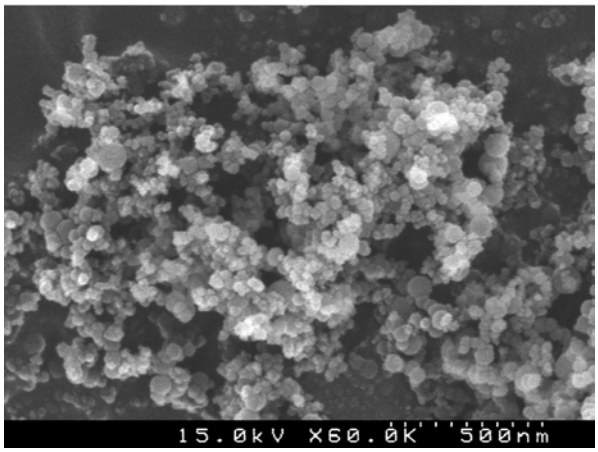

Fig. 5. SEM micrograph of the sample prepared from the plasma discharge into the air (low energy firing of 44 kJ).

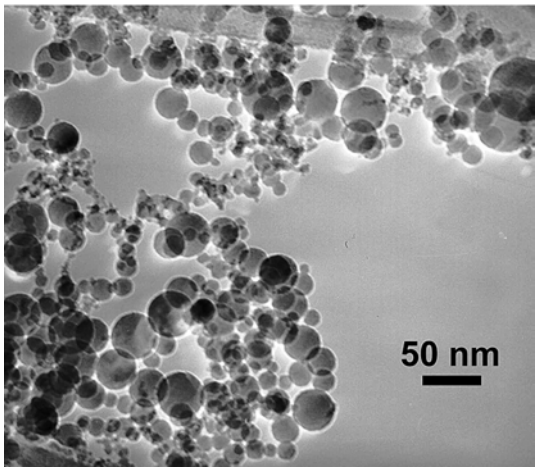

Fig. 6. TEM micrograph of the sample prepared from the plasma discharge into the air (low energy firing of 44 kJ).

Fig. 7 represents the XRD patterns of the samples collected from low and high energy firings. The composition is almost pure γ-phase alumina for the sample from the low energy firing. However, the alumina powder from the high energy firing contains small amounts of δ- and α-phase alumina, even though γ-phase is still dominant. One possible source of the α-phase, which is not transition alumina, could be the erosion of the alumina bore but, as shown in the XRD of lower energy firing, the eroded alumina bore material is likely to be dissociated into aluminum and oxygen species at the bore exit. However, there is a still possibility of incomplete dissociation of the bore material in high energy firing if shear erosion is severe due to the high energy deposition. A transformation from the less stable phase to the more stable phase is characterized by a decrease of surface area and larger particles, possibly over a diameter of 100 nm, which is likely to be the more thermodynamically stable form of alumina (δ- and α-phase) than the metastable γ-phase. It should be noted that a similar trend of γ-phase preference over more stable phases has been reported in other plasma-assisted techniques of alumina nanoparticle production [5, 12]. The formation of metastable phases in nanoparticle production by vapor condensation approaches is due to the homogeneous nucleation accompanied by the solidification of liquid droplets. It is understood that the quenching rate of metal vapor has a profound effect on the particle formation and, if the quenching rate is extremely high, amorphous alumina is expected [13]. However, in the present method, where the quenching rate is estimated to be approximately 10^5 K/s, synthesized nanoparticles have metastable crystalline structures. In all cases tested for material composition, no indication of unreacted aluminum has been found.

Particle size distributions of the alumina nanopowder collected were evaluated from the TEM micrographs

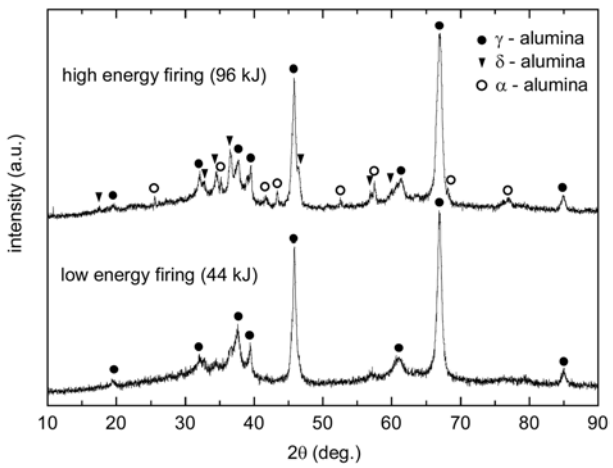

Fig. 7. XRD patterns of the samples prepared from the plasma discharge into the air.

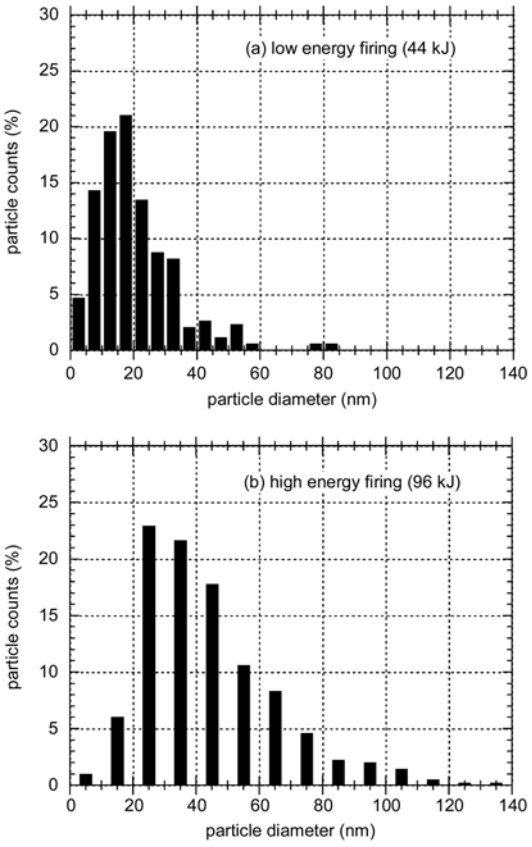

Fig. 8. Particle size distributions of alumina nanoparticles prepared in (a) low energy firing (44 kJ) and (b) high energy firing (96 kJ).

and are shown in Fig. 8, showing typical log-normal distributions. Surface mean particle diameters based on these size distributions are found to be 31 nm for the low energy firing and 55 nm for the high energy firing and this overestimation is due to the difficulty of identifying small particles particularly those below 10 nm.

In order to test the repeatability of the present method of nanoparticle production, several other cases of energy deposition in plasma discharge operations were carried out all with an atmospheric air condition in the reaction chamber but with varying the energy deposition in the plasma jet firing. As shown in Fig. 9, the energy deposition has a significant effect on the particle size in the synthesized nanopowder, although the effect becomes weaker with increasing energy deposition. At a higher energy deposition, erosion of the aluminum cathode and alumina bore is expected to increase and in turn yield more synthesized nanoscale alumina. In the present study, no attempt has been made to measure the production yield of nanopowder production due to the unsophisticated method of particle collection.

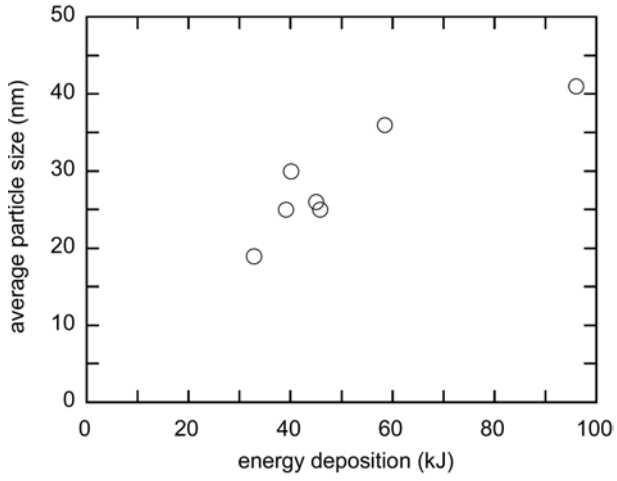

Fig. 9. Effect of deposited energy in the plasma discharge on the average particle size of the alumina nanoparticles collected.

Conclusions

An electrothermal gun has been used to produce nanocrystalline alumina particles by the reaction of the pulsed alumina plasma vapor discharge with the controlled background gas in the reaction chamber. Highly ionized aluminum vapor is created from the erosion of solid aluminum electrodes and discharged from the electrothermal gun in the form of high temperature, high velocity plasma jet, then it mixes and reacts with the oxygen content in the background gas, which is followed by subsequent rapid condensation to form ultra-fine alumina particles.

In the experiments, two cases of pulsed power with energy depositions of 44 kJ and 96 kJ were employed to synthesize the alumina nanopowder. High-speed video recordings of the plasma jet discharge in the reaction chamber revealed that turbulent mixing and major reaction between the aluminum plasma vapor and oxygen gas was delayed several milliseconds after an initial current discharge of 1 ms time duration.

Material characterization revealed that high purity γ-phase alumina was synthesized from the low energy firing of 44 kJ. SEM and TEM micrographs show spherical alumina particles mostly ranging between 5 and 50 nm with an average particle diameter of 26 nm based on their surface area. By contrast, the test with the high energy firing yielded larger size nanophase alumina particles of 41 nm average particle diameter and the XRD results show the synthesized powder is still mostly γ-phase but with a small amount of more thermodynamically stable forms such as δ- and α-phases.

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