Oxidation and Melting of Aluminum Nanopowders

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Recently, nanometer-sized aluminum powders became available commercially, and their use as potential additives to propellants, explosives, and pyrotechnics has attracted significant interest. It has been suggested that very low melting temperatures are expected for nanosized aluminum powders and that such low melting temperatures could accelerate oxidation and trigger ignition much earlier than for regular, micron-sized aluminum powders. The objective of this work was to investigate experimentally the melting and oxidation behavior of nanosized aluminum powders. Powder samples with three different nominal sizes of 44, 80, and 121 nm were provided by Nanotechnologies Inc. The particle size distributions were measured using smallangle X-ray scattering. Melting was studied by differential scanning calorimetry where the powders were heated from room temperature to 750 °C in an argon environment. Thermogravimetric analysis was used to measure the mass increase indicative of oxidation while the powders were heated in an oxygen-argon gas mixture. The measured melting curves were compared to those computed using the experimental particle size distributions and thermodynamic models describing the melting temperature and enthalpy as functions of the particle size. The melting behavior predicted by different models correlated with the experimental observations only qualitatively. Characteristic stepwise oxidation was observed for all studied nanopowders. The observed oxidation behavior was well interpreted considering the recently established kinetics of oxidation of micronsized aluminum powders. No correlation was found between the melting and oxidation of aluminum nanopowders.

Introduction

Nanosized aluminum powders have been produced and evaluated as reactive additives to propellants and explosives¹⁻³ as well as components of nanocomposite energetic materials.^{4,5} An accelerated reaction rate is generally due to an increase in the specific surface of the powder. It has also been suggested that the melting point depression reported to occur for metal nanoparticles⁶⁻¹¹ could result in an earlier aluminum ignition (triggered by accelerated oxidation) and therefore, in shorter ignition delays.^{12,13} However, experimental data on melting of aluminum nanoparticles are scarce, and it was recently shown that no correlation exists between melting and ignition or oxidation for micron-sized aluminum powders.¹⁴⁻¹⁶ The main objectives of this work are to characterize experimentally melting and oxidation of the nanosized aluminum powders. The effect of the particle sizes on melting and oxidation kinetics was specifically addressed. Instead of a common practice of representing each powder sample with a single average particle size, the experimental size distributions for different nanopowders were obtained and used directly for quantitative interpretations of the measurements.

Experimental Section

Particle Size Distributions. Three aluminum nanopowders with the respective BET particle sizes of 44, 80, and 121 nm

were provided by Nanotechnologies Inc., Austin, TX. For each "as received" powder, the particle size distributions (PSD) were determined using small-angle X-ray scattering (SAXS).^{17–19} During the SAXS fitting process, polydispersity was taken into account using a log-normal distribution. Two log-normal distributed populations had to be used to fit the experimental SAXS data for each analyzed nanopowder. While the shape of the size distributions was assumed, the mean modal diameters and widths of both log-normal distributions were allowed to vary freely during the fitting process. The experimental SAXS data with a best fit based on the double log-normal distribution are presented in Figure 1.

Specific parameters determined from the SAXS measurements describing the PSD are presented in Table 1. The normalized frequency function, P(D), of aluminum nanoparticle distributions that was used in the study to describe melting and oxidation of aluminum nano-powders is expressed as

$$P(D) = \sum_{k=1}^{2} W_k \frac{1}{D \ln(\sigma_k) \sqrt{2\pi}} \exp\left(-\frac{\left(\ln(D) - \ln(\langle D \rangle_k)\right)^2}{2 \ln^2(\sigma_k)}\right) \quad (1)$$

where *D* is the diameter of the aluminum core, which is a parameter measured by SAXS directly, the index *k* represents two log-normal distributions, W_k is a weight factor for each of those log-normal distributions, σ_k are the geometric standard deviations, and $\langle D \rangle_k$ are the geometric mean diameters. The aluminum powder manufacturers report the oxide layer thickness, h_{ox} , in the range of 1.8–3.5 nm.²⁰ It was assumed that "as received" powders had an oxide thickness of 1.8 nm, so

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Figure 1. Experimental SAXS intensity for three different aluminum nanopowders as a function of the scattering vector. Symbols with error bars represent experimental data; solid lines are the modeled intensities based on linear superposition of two log-normal particle size distributions.



Figure 2. Volume based PSD for different aluminum nanopowders. The vertical axis shows percent of a differential of cumulative volume distribution for aluminum core divided by the logarithm of the particle size. Therefore, the area under each normalized PSD curves equals 100%.

TABLE 1: Particle Size Distributions of the AlNanopowders Obtained from SAXS

	log-normal distribution params and weight factors		
BET particle size, μ m (powder ID)	geometric mean diameter, $\langle D \rangle$, nm	geometric standard deviation, σ , nm	weight factor
44	18.8	1.80	0.999 42
	129.2	1.71	0.000 58
80	33.4	1.75	0.999 936
	328	1.47	0.000 064
121	38.4	1.72	0.997 937
	196.6	1.48	0.002 603

that the particle diameters measured by SAXS and representing the metal core were corrected accordingly. Powders stored in the laboratory for the duration of this project (about 6 months) continued to slowly oxidize as was determined from the thermogravimetric measurements performed over this period of time with the same powder batches. This growth of oxide thickness and respective changes in the overall particle diameters were accounted for while interpreting the oxidation measurements as described below.

The volume-based distributions for the aluminum core diameters, as determined by SAXS and described by eq 1 and in Table 1, are presented in Figure 2. PSD for each powder is skewed to the right side because of the presence of relatively large particles represented by the second log-normal mode (see Table 1). These large particles produce a noticeable contribution when such volumetric processes as melting and oxidation are considered.

The presence of relatively large particles within the nanopowders used in this research is clearly seen from the transmission electron microscopy image shown in Figure 3. The image shows a particle with a diameter of about 150 nm in the nanopowder with the BET size of 44 nm. Transmission electron microscopy images serve here for demonstration purposes only because only



Figure 3. Transmission electron microscopy image of an Al nanopowder with BET particle size of $44 \ \mu m$.

a limited number of particles are available from such images. This limited number of particles is not statistically representative and cannot be used for assessment of the powder size distribution.

Thermal Analysis. Melting and oxidation of the powders were studied using a Netzsch Simultaneous Thermal Analyzer STA409 PC. The instrument was calibrated for temperature with the melting points of a set of metal standards resulting in a temperature accuracy of ± 1 °C.

To describe melting, differential scanning calorimetry (DSC) was performed in argon, heating powders up to 750 °C with a rate of 5 °C/min. The 35-45 mg samples were heated in alumina and platinum sample holders. To establish reproducible initial conditions for the DSC measurements, each sample was heated from room temperature to 300 °C at 20 °C/min and kept at 300 °C for about 30 min prior to the main heating program. During heating and melting, sintering can occur affecting the powder sample's geometry, location in the DSC sample holder, and the heat transfer in the DSC measuring head. To minimize such artifacts, three experiments were performed. In the first experiment, the powder was loosely packed in the sample holder. In the second test, the powder was pressed into a pellet. Finally, in the third experiment, the powder was mixed with alumina powder (Inframat Advanced Materials LLC, Farmington, CT, particle size ≈ 150 nm) in the 1:1 mass ratio, and the mixture was loosely packed in the sample holder. The results of all three types of experiments were generally consistent, while the most reproducible measurements were obtained with the mixed Al/ Al₂O₃ powders. These measurements are presented below.

Oxidation was characterized using thermogravimetric analysis (TGA). Samples of 25–40 mg contained in alumina crucibles were heated in an oxygen/argon environment (oxygen flow rate 10 mL/min, argon flow rate 50 mL/min) from room temperature to 1350 °C. Heating to higher temperatures, performed in a

limited number of experiments, did not result in any further weight increase. Two heating rates of 1 and 5 $^{\circ}$ C/min were used in the study.

Oxidation Modeling

Recently, oxidation of micron-sized aluminum powders was described considering formation of different polymorphs of Al_2O_3 .^{14–16} At different oxidation stages, the oxidation rates are limited by the diffusion resistance of different crystallographic modifications of alumina. The oxidation model described in detail elsewhere¹⁶ was modified in this work to account for the effect of particle size distribution on the diffusion and oxidation rates. After this modification, the model was used to predict the TGA curves expected for each powder sample while the PSD for each powder was obtained from SAXS measurements. All particles were assumed to be spherical.

Major Processes during Aluminum Oxidation. Initially, aluminum particles are covered by a thin layer of "natural" amorphous oxide, and it should be noted that recent research using prompt gamma neutron activation analysis²¹ and highresolution transmission electron microscopy²² showed that the amorphous oxide coatings on aluminum nanopowders include impurities of hydroxide, trapped water molecules, and boron. In addition, single crystalline layers were observed on the surface and in localized areas of the otherwise amorphous oxide. Such impurities as hydroxide are expected to become more significant for aged particles. However, addressing the effect of such impurities on the aluminum oxidation was beyond the scope of this paper. These effects, together with effects of specific surface morphology (e.g., nonspherical and agglomerated particles) and bulk impurities (e.g., iron, copper, and potassium detected by X-ray photoelectron spectroscopy²²) will certainly reduce the accuracy of the aluminum oxidation model¹⁶ that is also used in the present paper.

Neglecting the impurities present in the initial amorphous oxide layer it is simply assumed that at low temperatures its thickness increases. At elevated temperatures, the amorphous alumina transforms into a denser γ -Al₂O₃ polymorph. This phase transformation can reduce the thickness and the diffusion resistance of the oxide layer. For thin oxide layers observed at high heating rates, this phase change can also result in local discontinuities in the oxide coverage.^{14,16} Thus, the rate of oxidation accelerates rapidly until a continuous, polycrystalline layer of the γ -Al₂O₃ is produced. Note that the decomposition of any hydroxide phase would lead to a similar volume reduction, accelerating oxidation as well. As the temperature continues increasing, the layer of the γ -Al₂O₃ grows until crystallites of an even denser α -oxide start forming. Formation of a higher density oxide polymorph once again results in a reduction in the overall oxide thickness and the diffusion resistance of the oxide layer. An accelerated oxidation continues until the oxide layer transforms into a continuous, polycrystalline film. According to this model,^{14,16} five processes need to be analyzed to describe the oxidation quantitatively. In the order of their occurrence at the increasing temperatures, these processes are (1) growth of amorphous oxide, (2) the amorphous to γ -alumina phase change, (3) growth of γ -alumina, (4) the γ to α -alumina phase change, and (5) growth of α -alumina.

General Model Formulation. The mass of each alumina polymorph and the mass of metallic aluminum are computed as a function of time and temperature. To account for the effect of specific PSD, the computations are made for each particle size and then integrated over the PSD. According to the model, changes in the mass of each oxide polymorph can be caused by two different processes: a mass change $\dot{m}m^{\alpha x}$ due to the direct aluminum oxidation and a mass change \dot{m}^{tr} due to polymorphic phase transformations. Because of the accepted sequence of the polymorphic phase transitions: *amorphous* $\rightarrow \gamma \rightarrow \alpha$,¹⁴ the specific masses of the amorphous, γ -, and α -oxides, referred to by the subscripts am, γ , and α , respectively, are determined for each instant of time (or for each temperature) from the following equations:

$$\rho_{\rm am} \dot{V}_{\rm am} = \int [\dot{m}_{\rm am}^{\rm ox} - \dot{m}_{\rm am \to \gamma}^{\rm tr}] P(D) \, \mathrm{d}D \tag{2.1}$$

$$\rho_{\gamma}\dot{V}_{\gamma} = \int [\dot{m}_{\gamma}^{\text{ox}} + \dot{m}_{\text{am}\to\gamma}^{\text{tr}} - \dot{m}_{\gamma\to\alpha}^{\text{tr}}]P(D) \,\mathrm{d}D \qquad (2.2)$$

$$\rho_{\alpha} \dot{V}_{\alpha} = \int [\dot{m}_{\alpha}^{\text{ox}} + \dot{m}_{\gamma \to \alpha}^{\text{tr}}] P(D) \, \mathrm{d}D \tag{2.3}$$

$$\rho_{\rm Al} \dot{V}_{\rm Al} = -\frac{2\mu_{\rm Al}}{\mu_{\rm Al_2O_3}} \int [\dot{m}_{\rm am}^{\rm ox} + \dot{m}_{\gamma}^{\rm ox} + \dot{m}_{\alpha}^{\rm ox}] P(D) \, \mathrm{d}D \qquad (2.4)$$

where \dot{V} is the rate of volume change, ρ is density, and all the variables in the square brackets are functions of particle diameter. The temperature of aluminum particles, T, affecting the rates of mass change, \dot{m}_i , increases from room temperature at a constant rate used in the oxidation TGA experiments. The modeled TGA weight change was calculated by integrating eqs 2.1–2.4 over time numerically.

The rates of mass change due to direct oxidation were described by the model of diffusion for the rate-limiting species. To simplify the boundary conditions necessary to compute the diffusion mass flows, the model allows the direct oxidative growth of only one alumina polymorph at any given time. Specifically, at any given time only the alumina polymorph with the highest diffusion resistance, which is tracked during the calculations, is allowed to grow because of the direct oxidation. The phase transformations can occur simultaneously and may contribute to the growth of any coexisting alumina polymorph. Thus, if several alumina polymorphs coexist, each particle is surrounded by concentric shells of the respective oxide polymorphs. The spherical symmetry allows one to recalculate volumes of alumina and aluminum core for each specific particle size using equations similar to 2.1-2.4, but written for an individual particle, without the integration over PSD.

Diffusion-Limited Oxidation. For each polymorph, the rate of direct, diffusion-limited oxidation for a spherical oxide layer of outer diameter, D_i , is described using an Arrhenius type expression

$$\dot{m}_{i}^{ox} = \frac{1}{2}C_{i} \exp\left(-\frac{E_{i}}{RT}\right)\left(\frac{1}{D_{i-1}} - \frac{1}{D_{i}}\right)^{-1}$$
(3)

where the subscript i indicates the specific oxide polymorph, that is, amorphous, γ , or α alumina, subscript i-1 indicates the underlying substrate or "parent" material, which could be aluminum, amorphous, or γ alumina, respectively, C_i and E_i are the parameters describing the diffusion of rate-limiting species in different alumina polymorphs, and *R* is the ideal gas constant. The values of C_i , and E_i were the same as determined recently for the oxidation of micron-sized aluminum particles.¹⁶

Diffusion in Thin Oxide Layers. Additional assumptions were necessary to describe the oxidation kinetics when the oxide thickness was comparable to the size of individual γ - and α -oxide crystallites. When such crystallites are initially formed, the discontinuities in the oxide coverage are produced.^{14,16} The initial diffusion resistance of the newly formed γ - and α -oxide crystallites was neglected. A critical thickness for each of the

new growing layers of the γ - and α -oxide polymorphs was identified at which these layers stop behaving as individual crystallites and start producing diffusion resistance typical of respective continuous polycrystalline layers. These transition oxide thicknesses, introduced previously to describe oxidation of the micron-sized aluminum powders,¹⁶ were also used here. According to the model proposed in ref 16, the diffusion resistance of a new growing oxide layer increases linearly with the increase in the oxide thickness until a continuous, polycrystalline oxide coverage is formed. Further details are available in ref 16.

Polymorphic Phase Changes in Al₂O₃. The rate of mass increase, $m_{(i-1)\rightarrow i}^{tr}$, of the oxide phase i transformed from the oxide phase i-1 is described as

$$\dot{m}_{(i-1)\to i}^{\rm tr} = \pi D_{i-1}^2 \cdot \rho_{i-1} v_{(i-1)\to i} \tag{4}$$

where v is the velocity of the interface motion. The velocity is described using a phenomenological expression proposed in ref 16, in which the thermal kinetics are supplemented by the effect of the thickness of the parent layer of transition alumina, $h_{i-1} = \frac{1}{2}(D_{i-1} - D_{i-2})$

$$\nu_{(i-1)\to i} = F_{(i-1)\to i}T\left\{1 - \exp\left(-\frac{K_{(i-1)\to i}h_{i-1}}{RT}\right)\right\} \exp\left(-\frac{E_{(i-1)\to i}}{RT}\right)$$
(5)

The activation energies E for each specific phase transition, as well as parameters F and K, were determined earlier by processing the TGA data for the micron-sized particle.¹⁶

Initial Conditions. The initial volumes (and thus thicknesses) of both γ and α phases were equal to zero. The initial volumes of the amorphous oxide and aluminum core were considered as a function of PSD using the SAXS measurements and a sizedependent correction required to account for "aging" or oxidation of the powders stored in the laboratory. The overall mass of the initial oxide for the "aged" particles was determined from the total mass increase measured from the respective TGA curves acquired in the oxygen/argon environment. Thus, a specific correction was introduced for interpretation of each specific TGA experiment. The oxidation of powders during their storage was analyzed assuming a uniform, 1.8 nm, initial oxide thickness for "as received" particles of all sizes and using eqs 2.1, 2.4, and 3 while allowing the particle's temperature to remain at a constant room-temperature level. The growing thickness of the amorphous oxide layer was computed as a function of time until the total mass of the oxide layer matched the oxide mass inferred from the TGA measurements. The oxide growth rate was assumed to be limited by the diffusion of the reacting species at the storage temperature. An example of the resulting distribution of the oxide thickness over the particle diameter is shown in Figure 4. A similar distribution of the oxide thickness as a function of the particle diameter is expected for any aluminum nanopowder.

The calculations in which the diffusion rates depend on particle size (cf. eq 3) predict that the oxide thickness increases faster for the finer particles. This explains the decreased oxide thickness as a function of the particle diameter for particles greater than 10 nm. On the other hand, particles less than 10 nm (in the specific case shown in Figure 4) are already fully oxidized. For the fully oxidized particles, the thickness of the oxide layer is naturally limited by the particle diameter, so that a sharp peak is observed in Figure 4 for the particle diameter



Figure 4. Calculated initial thickness of the amorphous oxide layer as a function of the particle size for an aluminum nanopowder (BET diameter 80 nm) stored in the laboratory for a period of time.

corresponding to the largest fully oxidized particles. Extended aging will result in a slow increase of the oxide thickness for the decreasing branch of the curve (particles that are not fully oxidized) and a shift of the peak toward greater particle sizes. It is clear that the size-dependent "aging" effect is substantial only for the particles that are smaller than \sim 20 nm while it can be neglected for coarser particles.

Melting Models

Melting Temperature and Entropy Dependence on Particle Size. The effect of particle size on its melting temperature and latent heat of melting for nanosized metal particles has been extensively discussed in the literature. A model commonly quoted in recent papers dealing with aluminum nanopowders used in energetic materials,¹³ for example, was developed about five decades ago.⁶ That model describes the melting point, T_m , as a function of the particle diameter, D_p , and the oxide shell thickness h_{ox} , as

$$T_{\rm m} = T_{\rm b} \left[1 - \frac{4\sigma_{\rm sl}}{H_{\rm b}\rho_{\rm Al}(D_{\rm p} - 2h_{\rm ox})} \right] \tag{6}$$

where $T_{\rm b}$ is the melting temperature of bulk aluminum, $H_{\rm b}$ is the enthalpy of fusion of bulk aluminum, and $\sigma_{\rm sl}$ is the interfacial surface tension between the solid and the liquid. The difference in the molar volumes between solid and liquid aluminum was neglected.

More recently, a theoretical model of melting for nanocrystalline metal powder was developed by Jiang et al.^{8–10} It has been proposed that the melting point depends on the diameter of aluminum nanocrystals, assumed in our study to be equal to the diameter of particle aluminum core, as

$$T_{\rm m} = T_{\rm b} \exp\left(-\frac{2H_{\rm b}}{3RT_{\rm b}}\frac{1}{\left(\frac{D}{6l}-1\right)}\right) \tag{7}$$

where *l* is the length of the Al–Al atomic bond. Furthermore, it was suggested that for nanoparticles, the latent heat of melting, $H_{\rm m}$, depends on the particle diameter according to

$$H_{\rm m} = H_{\rm b} \exp\left(-\frac{2H_{\rm b}}{3RT_{\rm b}}\frac{1}{\frac{D}{6l}-1}\right)\left[1-\frac{1}{\frac{D}{6l}-1}\right]$$
(8)

Finally, processing the experimental results reported by Eckert et al.¹¹ suggests phenomenological dependencies for both the melting point (in K) and latent heat of melting (in kJ/mol) as functions of the aluminum core diameter (in nm):

$$T_{\rm m} = 977.4 - \frac{1920}{D} \tag{9}$$

$$H_{\rm m} = 14.705 - \frac{177.49}{D} \tag{10}$$

The experimental data presented in ref 11 limit applicability of the trends given by eqs 9 and 10 for the particles with diameters in the range of 12.07 nm < D < 43.24 nm. For larger particles, $T_{\rm m} = T_{\rm b}$ and $H_{\rm m} = H_{\rm b}$. For particles with the metal core smaller than 12.07 nm, the latent heat of melting is reported to be negligible.¹¹

Modeling of Experimental DSC Signal. Three different melting models introduced above were used together with the experimental PSD to quantitatively predict the DSC signals expected while different powder samples melt. Each calculation was compared to a specific DSC run. The correction for the initial oxide thickness as a result of aging for each specific DSC run was made in the respective calculations using the procedure described above and the results of the concurrent TGA measurements. Equations 6, 7, and 9 represent functional dependence of the melting temperature on the particle diameter. Each of these equations was converted into a respective dependence of the aluminum core diameter as a function of the melting temperature, $D = D(T_m)$. The converted functional dependencies and their temperature derivatives dD/dT were used to predict the DSC signal directly. The DSC experiments were performed at a constant heating rate, β , so that the DSC signal, Q, detected at each specific temperature, T, was calculated as

$$\dot{Q} = M_{\rm s} P(D) \frac{\pi}{6} D^3 H_{\rm m}(D) \frac{dD}{dT} \beta$$
(11)

where M_s is the parameter accounting for frequency function normalization, proportional to the mass of the aluminum metal in the analyzed nanopowder sample.

Results and Discussion

Experimental DSC curves showing the melting endotherms for different powders are shown in Figure 5 together with the TGA curves showing the weight increase for the same powders as a result of oxidation.

For all powders, the oxidation is observed to begin at the temperatures substantially lower than the onset for the melting endotherm (occurring at around 570 °C for all powders). Thus, no correlation between melting and oxidation is observed, similarly to the results for the micron-sized Al powders.^{14–16} The substantial difference in the slopes of the DSC curves before and after melting is most likely explained by the change in the powder morphology as a result of its melting. The change in morphology affects the heat transfer within the DSC sample holder and, therefore, the baseline of the measurement.

Comparisons of the experimental TGA curves with the curves predicted by the recently developed aluminum oxidation model are shown in Figure 6. The absolute measured mass increase becomes smaller for the same particles used in different experiments after increasingly longer storage periods, indicating that oxidation did occur during the storage. At the same time, the final mass increases for the calculated and experimental TGA curves always coincide because of the discussed above correction for the initial oxide layers for the powders stored in the laboratory during different periods of time. The calculations, in general, reproduce well the shapes of the experimental TGA curves. The shift between the TGA curves as a function of the heating rate is also well described.



Figure 5. DSC and TGA curves measured for three aluminum nanopowders in argon and oxygen, respectively. Both sets of curves were acquired at a heating rate of 5 $^{\circ}$ C/min.



Figure 6. Comparison of experimental TGA curves with results of the oxidation modeling.

There are, however, minor but systematic discrepancies between the predicted and calculated curves, as shown in Figure 6. The calculated TGA curves are extremely sensitive to the specific shape of the particle size distribution and particle surface morphology. It is suggested that the disagreement between the presented oxidation theory and experiments is within the ranges expected on the basis of the accuracy with which the particle size distributions are determined.

Comparisons of the experimental DSC melting curves with the curves predicted to describe respective measurements by different melting models of metal nanopowders are presented in Figure 7. No close agreement between experiment and any of the tested melting models was observed; however, the overall shape of the melting endotherm was predicted by all the models. In particular, it is interesting that the experimental endotherms have at least two peaks, and this overall shape is generally predicted considering the bimodal size distributions obtained from SAXS (see Table 1). Note that according to eqs 9 and 10,¹¹ only a fraction of the powder is predicted to melt before $T_{\rm b} = 660$ °C is reached. The rest of the powder, as noted in Figure 7, is expected to melt at a constant temperature of $T_{\rm b}$,



Figure 7. Experimental and computed DSC curves showing melting of aluminum nanopowders.

so that respective calculations for the melting endotherms could not be performed and are not shown in Figure 7.

It was found that the shapes of the predicted curves are very sensitive to the specific type of the particle size distribution, for example, bimodal versus single mode log-normal distribution. The melting curves can further depend on the specific surface morphologies of the used nanoparticles that could affect the sizes of melting nanodomains.

Conclusions

Melting and oxidation of aluminum nanopowders are studied experimentally and the results are compared with the predictions of several models published to date. Experiments showed that the oxidation and melting onsets of the heated aluminum nanopowders do not correlate consistently with the conclusion made earlier for the micron-sized aluminum powders. The melting of nanopowders starts at a lower temperature than the melting point of bulk aluminum; however, existing models describe the effect of the particle size on the melting point depression only qualitatively. Detailed analysis of the particle size distributions and surface morphology is needed for further quantitative verification of any related models. A recent oxidation mechanism taking into account polymorphic phase changes in the Al₂O₃ layer describes oxidation of the nanopowders satisfactorily. The particle-size dependent oxidation model developed in the study was successful in describing the experimental TGA curves. The same model was used to evaluate the particle size dependent thickness of the oxide layer produced on the aluminum nanopowders during their storage at room temperature. Observed minor inconsistencies between predictions of the proposed oxidation model and TGA measurements can be related to the extreme sensitivity of the oxidation rates to the specific shape of the particle size distribution that was described in this work by a superposition of two log-normal functions.

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