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Metal Nanopowders

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Foreword

Interest in studying the combustion of metal powders dramatically raised since Russian scientists Kondratyuk and Tsander suggested the use of metals as energetic additives to rocket fuels at the beginning of the twentieth century. Since that time, it is obvious that an increase in the dispersion of flammable substances participating in heterogeneous combustion processes leads to an increase in rate and heat of combustion. The major energy contribution belongs to the process of oxidation, which is also bound up with powder dispersion and purity. Burning of metal nanopowders is accompanied by new physical and chemical laws (such as high reactivity under heating, threshold phenomena, formation of nitrides in air), which allow to fully appreciate the advantages and disadvantages of nanopowders when used in fuel systems.

Widespread use of metal nanopowders is currently hampered by the lack of enough advanced technology for their preparation, certification, and standardization procedures, instability during storage, and subjective factors: the possible toxicity of nanopowders, investment risks, cost of nanotechnologies, and so on. Therefore, the main objective for the authors is to inform a wide readership of fundamental and applied studies on the processes of oxidation and combustion of metal nanopowders.

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Introduction

Stabilization of low-dimension structures, especially nanosized ones, and their use in the heterogeneous chemical reactions as nanopowders allow considering high specific surface as an independent thermodynamic parameter along with the temperature, pressure, concentration of reactants, and so on. New characteristics of 2D nanomaterials are well known – the thermal conductivity of graphene \((5000 \text{ W (m K)}^{-1})\) with \(1000 \text{ m}^2 \text{ g}^{-1}\) specific surface exceeds those for metals in a factor \(10\) \([1]\). The use of the advantages of high specific surface of 3D nanostructures – nanopowders in catalysis, oxidation, and combustion results in high rates of heterogeneous reactions and reduction in activation energies of ignition due to the small size of solid reactants. The laws of classical chemistry and physics are little applicable to the analysis of processes with metal nanopowders. An example of such a system is the burning of the composition nanoAl/nanoMoO\(_3\) at the rate of about \(1 \text{ km s}^{-1}\) \([2]\).

In USSR, metal ultrafine (in fact, nano-) powders with reproducible properties were first obtained during World War II. In the 1960s and 1970s, numerous works were carried out on metal nanopowder production by electrical explosion of wires \([3]\), evaporation-and-condensation method \([4]\), and the technologies of metal nanopowder application for nuclear synthesis in the USSR and the US. In 1977, the result of these works was published in Morokhov’s book \([5]\), where the methods for metal nanopowder production by thermal decomposition of salts were viewed. In Western Europe and the US, the term nanocrystalline material appeared and spinned off after the Gleiter’s publication in 1980 \([6]\).

Since the discovery by Yu. Kondratyuk and F. Tsander in 1910 \([7]\), the possibilities of powdery metal being used as an additive in energetic materials and as the reagents for self-propagating high-temperature synthesis \([8]\) were intensively studied. Several books (e.g., the work of Pokhil et al. \([9]\) and Sammerfield \([10]\)) were published, where the laws of combustion of micron-sized metal powders (5–500 \(\mu\)m) in high-temperature oxidizing environments were discussed. The study of the laws of combustion of powderized metals was done mainly for Al, Be, Mg, Ti, Zr, and B. The lack of micron-sized metal powders were detected during the first test of metallized fuels in the 1940s: an agglomeration of particles (especially for aluminum and magnesium) in the heating zone of energetic material, a low degree of metal
reaction in the vapor phase (incomplete combustion), significant biphasic loss of a specific impulse (15% or more for the compositions containing 20–25 wt% Al) [9].

In the 1970s, Zeldovich and Leipunsky et al. [11] showed one of the approaches to reduce this lack by using low-sized metallic particles for fuels and combustion catalysts, in particular, metal nanopowders. This book summarizes the efforts of several teams over the world to realize those ideas.

The revitalization of the use of metal nanopowders in materials science and engineering became further possible in the 1990s, when the technologies for the large-scale production of those materials became available. Nowadays, tons of rather inexpensive metal nanopowders are produced in several countries for different technological applications, while the problems of their standardization, storage, handling, toxicity, correct application, and so on, are still unsolved.

The idea of this book is also to show the true picture of the properties of metal nanopowders and, correspondingly, their application avenues. The “romantic atmosphere” around nanomaterials and metal nanopowders accordingly should be left in the twentieth century forever. Nanoparticles and, especially, metal nanoparticles are very “capricious” technological raw materials with metastable physical and chemical properties in many cases, because nanometals (in addition to small particle size) show very high reducing properties: nanoCu react similarly to bulk Zn – release the hydrogen from acids, nanoAl show the properties of bulky alkali metals – react with water under room temperature, and so on.

Special scientific and engineering interests represent the new fundamental laws of combustion for the metal nanopowders, analysis of the combustion regimes, and intermediate and final burning products reported in this book. Excited by the experimental works of Ivanov and Tepper [12], scientists worked in the direction of nanometals application in energetic materials intensively during the past decade and the most valuable results are presented in this book.

In conclusion, we want to underline that the study of industrially available metal nanopowders allowed opening previously unknown laws and they will open the significant application prospects in science and technology of the twenty-first century.

Alexander Gromov
Ulrich Teipel

References


1

Estimation of Thermodynamic Data of Metallic Nanoparticles Based on Bulk Values

Dieter Vollath and Franz Dieter Fischer

1.1

Introduction

It is a well-accepted fact: the temperature of phase transformation is particle-size dependent. In general, this dependency is described as

\[ T_{\text{trans-nano}} = T_{\text{trans-bulk}} - \frac{\alpha}{d} \]  

(1.1)

In Equation 1.1, the quantities \( T_{\text{trans-nano}} \) and \( T_{\text{trans-bulk}} \) stand for the transformation temperature of nanoparticles and the bulk material, respectively, \( d \) for the particle diameter, and \( \alpha \) is a constant value depending on the entropy of transformation and the difference of the surface energy in both phases [1]. The same description, as proved for phase transformations, was found to be valid for the enthalpy of phase transformations. As typical examples, experimental results obtained for aluminum particles were given by Eckert [2], for tin particles by Lai et al. [3], or by Suresh and Mayo [4, 5] on yttrium-doped zirconia particles.

The range of particle sizes where Equation 1.1 is valid is limited. In the case of larger particles, Coombes [6] has shown that these have a surface layer of about 3 nm, where melting starts. As long as this surface layer dominates the behavior of the particles, Equation 1.1 cannot be applied. The existence of such a surface layer was also shown by Chang and Johnson [7] by theoretical considerations, concluding that this surface layer is less ordered than the center of the particles. As it was shown by Kaptay [8], the thickness of this premelting layer can be estimated by the rules of classical thermodynamics. Therefore, the assumption of a surface layer where melting starts is well justified. Now, one may ask if there is also a lower limit of particle sizes, below which Equation 1.1 is not applicable. Experimental results suggest this. Figure 1.1 displays the melting temperature of gold nanoparticles according to Castro et al. [9]. In this graph, the melting temperature is plotted versus the inverse particle size. According to Equation 1.1, one has to expect a linear relation.

The experimental data of Castro et al. may be separated into two ranges: Range I, which follows Equation 1.1 and a separated Range II, which is far off from the expected value. A linear fit of the experimental data in both ranges delivers an
1 Estimation of Thermodynamic Data of Metallic Nanoparticles Based on Bulk Values

Figure 1.1 Experimental data for the melting temperature of gold nanoparticles, according to Castro et al. [9], together with linear fits plotted versus the inverse particle size. This graph shows clearly two separated ranges of the melting temperature: at larger particles, a range following Equation 1.1 (Range I) and a second range with particle-size-independent temperature (Range II).

intersection at an inverse particle size of 0.62 nm\(^{-1}\), which is equivalent to a particle size of 1.6 nm. Obviously, for particle sizes below this intersection, Equation 1.1 is no longer valid. Such a phenomenon or similar ones are quite often described; as, for example, in the case of sodium particles [10]. Well in line with the above-described phenomenon, found for gold and sodium particles, are experimental results of Shvartsburg and Jarrold [11] on small tin particles consisting of 19–31 atoms, exhibiting melting points significantly higher than those of the bulk material. Besides a reduction of the melting temperature, close to melting or crystallization, additional phenomena are observed. Oshima and Takayanagi [12] found in 6 nm tin particles crystalline embryos with sizes around 1.5 nm. It is remarkable that this size is in the range of the limitation of Equation 1.1, as was found in the case of the melting of gold particles.

1.2 Thermodynamic Background

A general analysis of these phenomena needs detailed quantum mechanical studies. However, in most cases, one is interested in just a first approach using thermodynamic data of metallic nanoparticles. It is the aim of this chapter to show a simplified approach in this direction. The most important tool for any analysis of this kind is classical thermodynamics. Certainly, as this tool describes continuous systems, such an approximation cannot deliver phenomena depending on the quantum nature of the cohesion energy of small particles, or, in other words, magic particle sizes, superatoms, or jellium shell concepts cannot be expected as the result. These phenomena are excluded.
To analyze phase transformations, a detailed knowledge of the thermodynamic data of the materials in question is necessary. In addition, in the case of nanoparticles, knowledge of the surface energy in both phases is of great importance. As typical and well-studied examples for a phase transformation, melting, and crystallization were selected. In the following considerations, for reasons of simplicity, the minor changes of geometry and density are neglected. Generally, in the proximity of the melting point, the difference of the free enthalpy

\[ G_{m-nano} = G_{\text{liquid-nano}} - G_{\text{solid-nano}} \]

at the temperature \( T \) are

\[ G_{m-bulk} = G_{\text{liquid-bulk}} - G_{\text{solid-bulk}} \] (1.2a)

The quantity \( H_m \) is the enthalpy and \( S_m \) the entropy of melting, both with the additional subscript “nano” or “bulk.” The term \( \Delta \gamma \) stands for the difference in the surface energy in the liquid and solid states. The quantity \( A \) represents the surface area per mol of nanoparticles. It is important to note that the quantities in Equations 1.2 are the differences of the thermodynamic quantities observed during the melting process.

\[ H_m = H_{\text{liquid}} - H_{\text{solid}} > 0 \]

\[ S_m = S_{\text{liquid}} - S_{\text{solid}} > 0 \]

\[ \Delta \gamma = \gamma_{\text{liquid}} - \gamma_{\text{solid}} < 0 \] (1.3)

In the case of bulk materials, the surface energy term \( \Delta \gamma A \) of Equation 1.2b is generally neglected but it is of relevance in the case of nanoparticles.

For lack of better data, in most cases, the material data of the bulk material \( H_{m-bulk} \) and \( S_{m-bulk} \) are used for nanoparticles, too, yielding

\[ G_{m-nano} = H_{m-bulk} - T S_{m-bulk} + \Delta \gamma A \] (1.4)

Setting \( G_{m-nano} = 0 \) leads to the well-known reduction in the melting point of nanoparticles \( T_{m-nano} \) in comparison with the one of the bulk material, \( T_{m-bulk} \), as was described for the first time more than a hundred years ago by Pawlow [13] using \( G_{m-bulk} = 0, H_{m-bulk} = T_{m-bulk} S_{m-bulk} \), and neglecting \( \Delta \gamma A \) for the bulk material, and more recently in [14–16] as

\[ \frac{T_{m-nano}}{T_{m-bulk}} = 1 + \frac{\Delta \gamma A}{T_{m-bulk} S_{m-bulk}} = 1 - \left| \frac{\Delta \gamma A}{T_{m-bulk} S_{m-bulk}} \right| \]

\[ = 1 - \left| \frac{\Delta \gamma}{T_{m-bulk} S_{m-bulk}} \right| \frac{6M}{\rho d} = 1 - \left| \frac{\Delta \gamma}{H_{m-bulk}} \right| \frac{6M}{\rho d} \] (1.5)

In Equation 1.5, \( M \) stands for the molecular weight and \( \rho \) for the density of the particles. To visualize the general trend in the reduction of the melting temperature with decreasing particle size, the use of the absolute value of the fraction \( |\Delta \gamma / H_{m-bulk}| \) is the only correct way in the case of melting and crystallization.
As already mentioned, the derivations leading to Equation 1.5 assume that it is allowed to use bulk data for nanomaterials: however, this is problematic in the case of nanoparticles. The following gives a series of indications.

In a review on the melting of solids, Mei and Lu [17] devote a whole chapter to abnormal size effects on melting. Most interesting in this context are experimental findings of Shvartsburg and Jarrold [11] reporting that tin clusters consisting of 19–31 atoms exhibit melting points significantly above that of the bulk material. Molecular dynamic (MD) simulations for clusters of Cₙ, Siₙ, Geₙ, and Snₙ clusters for n ≤ 13 by Lu et al. [18] also revealed melting points significantly above that of the bulk materials.

- The material data of nanoparticles differ from those in bulk materials. For example, Vollath et al. [19] found drastic changes in the thermodynamic data of phase transformations in nanoparticulate zirconia, leading in the case of small particles to a change in the phase sequence with respect to temperature being reversed. An analogous phenomenon was found by Ushakov et al. [20] for pure and La-doped zirconia and hafnia nanoparticles with a diameter of 5–6 nm, where, at room temperature, the amorphous phase was more stable than the tetragonal one, in contrast to the general opinion that amorphous particles are the least stable ones.

- Even more dramatic is the influence on surface energy. There are experimental indications for a six times larger surface energy for nanoparticles of gold [21] and silver [22] compared to the bulk values. However, the model leading to such an evaluation of these experiments is seriously questioned [23, 24]. An increase in the surface energy by a factor of roughly two for aluminum nanoparticles was predicted in a theoretical study by Medasani and Vasiliev [25]. Both results contradict theoretical estimates that find a reduction in the surface energy with decreasing particle size [23, 24].

To estimate the thermal behavior of nanoparticles, knowledge of thermodynamic quantities and surface energy is essential. Therefore, it is the goal of this contribution to present proper and reliable approaches to estimate the thermodynamics of nanoparticles based on bulk data.

1.3
Size-Dependent Materials Data of Nanoparticles

For quite some time, there have been approaches to estimate the thermodynamic data of nanoparticles as a function of their size. Tolman [26, 27] presented such a relation for the surface energy as

\[ \gamma_{\text{nano}} = \frac{\gamma_{\text{bulk}}}{(1 + (4\delta/d))} \]  

(1.6)
The quantity $\delta$ is the so-called Tolman length. Das and Binder [28] generalized the Tolman relation to a wider applicable equation of type

$$\gamma_{\text{nano}} = \frac{\gamma_{\text{bulk}}}{(1 + 8(\tilde{l}/d)^2)^{1/4}}$$  \hfill (1.7)

In Equation 1.7, the quantity $\tilde{l}$ is again a characteristic length. However, Equation 1.7 was developed not for a free surface but an interface between two coexisting phases. A further relation, appraised as a “universal” relation, was reported by Guisbiers [29] in the form of

$$\xi_{\text{nano}} = \xi_{\text{bulk}} \left(1 - \left(\frac{\alpha}{d}\right)^{1/2}\right)^{1/2}$$  \hfill (1.8)

Guisbiers argues that this relation is valid for the material property $\xi$, which may be the melting temperature, Debye temperature, superconducting temperature, Curie temperature, cohesive energy, activation energy of diffusion, or vacancy formation energy. The quantity $\alpha$ is a material constant with the dimension of a length, and $s$ is a positive number depending on the material property. For $s = 1/2$ and $\alpha/d \ll 1$ Equation 1.6 and Equation 1.8 are practically equivalent. Furthermore, Equation 1.5 for the melting temperature obeys relation 1.8 with $s = 1/2$.

A more sophisticated relation for $\gamma_{\text{nano}}$ compared to Equation 1.8, based on the cohesive energy of nanocrystals, was reported by Lu and Jiang [23, 24] and Ouyang et al. [30], as

$$\gamma_{\text{nano}} = \gamma_{\text{bulk}} \left(1 - \frac{d_0}{d - d_0}\right) \exp\left(-\frac{d_0}{d - d_0}\right)$$  \hfill (1.9a)

The quantity $d_0$ is the “smallest size” of $d$ if this equation is valid. For $d/d_0 \gg 1$, Equation 1.9a can be rewritten as

$$\gamma_{\text{nano}} \approx \gamma_{\text{bulk}} \left(1 - \frac{d_0}{d - d_0}\right)^2$$  \hfill (1.9b)

and as a further approximation as

$$\gamma_{\text{nano}} \approx \gamma_{\text{bulk}} \left(1 - \frac{d_0}{d}\right)^2$$  \hfill (1.9c)

Equation 1.9c agrees again with Equation 1.8 for $s = 1/4$.

A different physical approach was reported by Li [31], using a layer-by-layer structure of the reference crystal from which the nanoparticle is cut out. This concept leads to an extremely complicated relation, which yields for $d_0/d \ll 1$ the same approximation as Equation 1.9c.

With respect to the melting point of nanomaterials $T_m^{\text{nano}}$, the thermodynamic approach of Letellier et al. [15, 16] should be noted. These authors have concluded the same tendency as shown in this chapter (Equation 1.5)

$$\frac{T_m^{\text{nano}}}{T_m^{\text{bulk}}} = 1 - c \left(\frac{d_0}{d}\right)^{1/2}$$  \hfill (1.9d)
However, they introduce also as a conceptual extension a positive exponent \( s \) to the quantity \( 1/d \) as \((d_0/d)^s\) with \( d_0 \) being a reference quantity and \( c \), a positive constant factor. They report a value of \( s = 0.79 \) for lead nanoparticles and \( 1.20 \) for tin nanoparticles.

Safaei and Attarian Shandiz [32] published a model for the melting entropy of metallic nanoparticles, based on the methods of statistical physics. It is important to emphasize that their final formulae for the entropy of melting and the melting temperature confirm the earlier work by Jiang and Shi [33, 34], who developed, on the basis of Mott’s equation for the melting entropy, a model for size-dependent melting temperature and entropy. Using an earlier approach to calculate the melting temperature of nanoparticles [35], Attarian Shandiz and Safaei [36] derived the same relations as Jiang and Shi [33, 34] for the melting temperature of metallic nanoparticles. The special feature of these derivations may be found in the fact that the final formulae depend on the thermodynamics and the crystal structure of the bulk material only. Furthermore, this approach inherently incorporates the influence of the surface energy. Therefore, this term no longer appears explicitly in the further equations.

Neglecting the electronic contribution, according to Attarian Shandiz and Safaei [32, 36], the ratio of melting temperatures is given by

\[
\frac{T_{m\text{-nano}}}{T_{m\text{-bulk}}} = 1 - (1 - q) \frac{2d_0}{d + d_0}
\]  

(1.10)

In Equation 1.10, \( d_0 \) stands for a critical particle size, where the particle consists of surface atoms only. It is important to point out that, from its derivation, Equation 1.10 already contains the influence of the difference of the surface energy. From its definition, \( d_0 \) depends on the crystal structure of the particle. Attarian Shandiz and Safaei [36] give a table of this quantity for different lattices, for example, for the fcc structure \( d_0 = 2.45 \cdot \delta \), where \( \delta \) stands for the diameter of one atom in the metallic environment. It is obvious that a table as in [36] for \( d_0 \) is applicable only in exceptional cases where the structure of the smallest particle is identical to the bulk structure. This assumption is not necessarily correct; for example, for gold, see Tian et al. [37]. Therefore, in many cases, it may be necessary to fit the parameter \( d_0 \) with experimental data. The quantity \( q = Z_S/Z_V \) is the ratio of the coordination numbers at the surface, \( Z_S \), and in the volume, \( Z_V \), of the bulk material. For bulk materials and larger particles, \( q = 0.5 \) is valid. Comparing calculated values with different results from the literature led Attarian Shandiz and Safaei [35, 36] to the conclusion that in the case of very small particles, a value \( q = 0.25 \) is more appropriate. This finding is well in line with a study on coordination numbers as a function of particle size and structure by Montejano et al. [38]. Therefore, a fit function was developed, which gives for the bulk material a value \( 0.5 \) and which decreases to \( 0.25 \) for the particle size \( d_0 \). Hence, it may be appropriate to select an expression such as

\[
q = 0.5 \frac{d}{d + d_0}
\]  

(1.11)