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Size-dependent hysteresis and phase formation kinetics during temperature cycling of metal nanopowders

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Abstract

We present a description of the evolution of a polymorphically transforming metal nanoparticle ensemble subjected to a temperature cycling with constant rates of temperature change. The calculations of the time dependence of the volume fraction of the new phase show the existence of size-dependent hysteresis and its main features. The statistical analysis makes it possible to introduce and determine the size-dependent superheating limit and supercooling limit.

1. Introduction

Nanopowder particles have found wide technological applications in modern industry, and their physical properties have become one of the critical concerns for new applications [1]. From this point of view the thermal stability of such particles is a subject of intense contemporary interest [2]. The synthesis of nanoparticles is not a simple task, however, numerous techniques have been developed for it [2–5]. Yet, despite the widely acknowledged importance, the understanding of the specific features of the evolution of phase transitions and hysteresis behaviour in such systems is far from being complete [6].

First-order phase transition experiments under changing external fields exhibit hysteresis phenomena related to supercooling and superheating [7, 8]. For example, a well-expressed heating–cooling hysteresis of Bi nanoparticles embedded in a bulk alkali germanate glass has been studied by high resolution transmission electron microscopy. It was shown that it can be related to the melting and solidification of the Bi nanoparticles. The temperature width of the hysteresis cycle is found at about 40% of the bulk Bi melting temperature [14].

Different results are reported in the literature concerning the width of the hysteresis loop. For example, the width of

the hysteresis loop for a polymorphic transition in the CdSe nanostructured system turns out to be almost independent of nanocrystal size [9, 10]. Other kinetic models and simulations for the ensemble of binary nanoparticles predict a considerable increase in the width of the hysteresis loop with increasing particle size as well as a decrease. Which of the mentioned effects will occur depends on the mechanism of the nucleation of the new phase [11–13]. The individual nucleation events observed in nanoscale vapour–liquid–solid growth for the Au–Si system provide us with a picture of reproducible heterogeneous nucleation of catalyst particles at the edge of the droplets [15]. Hereby the study of critical supersaturation required for nucleation does not give observable size effects. The melting behaviour of Ge nanocrystals embedded within SiO₂ is evaluated using *in situ* transmission electron microscopy. The melting-point hysteresis is observed at about 17% and is nearly symmetric about the bulk melting point [16].

In the study reported here, first-order phase transitions in ensembles of nanoparticles are discussed, specifically targeting polymorphic transitions in Fe nanoalloys undergoing temperature cycling. Dilatometric curves of the transformations α -Fe (bcc) $\leftrightarrow$ γ -Fe (fcc) in sintered powders of industrial particle sizes, 10–100 μ m, produced by comminuting 0.08% C steel welding wire in an eddy mill, show that the specimens

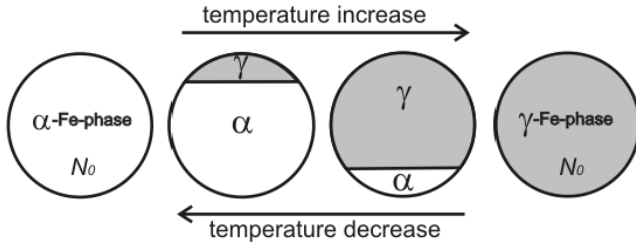


Figure 1. Model of complete α -Fe $\leftrightarrow$ γ -Fe phase transitions in nanoparticles due to heterogeneous nucleation, profile of phases along the diameter: on the left side—initial nanoparticle with α -phase inside, on the right side—the same particle after the polymorphic α -to- γ transition. N_0 is the number of atoms in a given particle of radius R with the lens-type new phase (grey colour).

sintered from the coarse powder are characterized by the largest temperature hysteresis loop and the least permanent compression [17]. In our previous analysis of the behaviour of such Fe nanopowders, nucleation of the new phase was assumed to occur inside and at the external boundaries of the existing nanoparticles. It was assumed, in addition, that the aggregates of the new phase are of spherical shape for both considered cases [18]. The kinetics can be expected to proceed in a different way if the nanoparticles transform via different modes, for example, via a nonspherical heterogeneous mode. Experiments show that there are many other cases where the growth of the new phase occurs at the surface of the nanoparticle and looks like epitaxial growth with lens-type new phase [15]. That is the case we deal with in the present paper.

First we develop a thermodynamic model of heterogeneous phase formation in an isolated nanoparticle (section 2), then we introduce the kinetic numerical model. The solution of the model predicts the existence of a size-dependent hysteresis and its peculiarities (section 3). Section 4 contains the summary and conclusions.

2. Thermodynamic analysis

Let us consider the case of phase transformations between the γ -Fe and α -Fe crystallographic phases (figure 1). Fe can exist in three main crystallographic modifications: α -phase (bcc) within the temperature interval $T < 1183$ K, γ -phase (fcc) for $1183 \text{ K} < T < 1665$ K and δ -phase for $T > 1665$ K up to the melting point.

Let N_0 be the number of atoms in one particle with radius R . At fixed temperature T , the total Gibbs free energy, G_α of the initial α -Fe-phase nanoparticle is given by

$$G_\alpha = N_0 g_{\alpha\alpha} + S_\alpha \sigma_\alpha. \quad (1)$$

In this equation, $g_{\alpha\alpha}$ is the bulk Gibbs free energy per atom of the α -phase, σ_α is the specific surface energy (energy per unit of area), $S_\alpha = 4\pi R^2$ is the surface area.

In a similar way, one can write the Gibbs free energy of the transformed γ -Fe-phase nanoparticle:

$$G_\gamma = N_0 g_{\gamma\gamma} + S_\gamma \sigma_\gamma. \quad (2)$$

Here $g_{\gamma\gamma}$ is the bulk Gibbs free energy per atom of the γ -phase, σ_γ is the specific surface energy and $S_\gamma = 4\pi R^2$ is the surface area of the γ -phase.

When the new γ -Fe phase nucleates, the Gibbs free energy dependence $G_{\alpha\gamma}$ has to be written for the two-phase configurations shown in figure 1. The change of the Gibbs free energy $\Delta G(N_\gamma)$ of the nanoparticle related to the formation of a new nucleus is then:

$$\Delta G(N_\gamma) = G_{\alpha\gamma} - G_\alpha = N_\gamma (g_{\gamma\gamma} - g_{\alpha\alpha}) + S'_\gamma \sigma_\gamma + S_{\alpha\gamma} \sigma_{\alpha\gamma} + (S'_\alpha - S_\alpha) \sigma_\alpha. \quad (3)$$

Here, N_α and $N_\gamma = N_0 - N_\alpha$ are the numbers of atoms in the α -Fe and γ -Fe phases, respectively; $\sigma_{\alpha\gamma}$ and $S_{\alpha\gamma}$ are the corresponding specific interfacial energy and area at the boundary of the α -Fe and γ -Fe phases. The quantities S'_γ and $S'_\alpha = S_\alpha - S'_\gamma$, are the external surface areas of the corresponding phases of the transforming $\alpha + \gamma$ -phase particle.

Let us now visualize the dependence of ΔG on N_γ at different fixed values of T and N_0 . Taking into consideration the set of parameters published in [19–26], it is possible to evaluate the Gibbs free energy of the α -Fe $\leftrightarrow$ γ -Fe transitions at isobaric conditions: $\sigma_{\gamma\alpha} = 8 \times 10^{-2} \text{ J m}^{-2}$, $\sigma_\alpha = 2.21 \text{ J m}^{-2}$, $\sigma_\gamma = 2.17 \text{ J m}^{-2}$, the volume density of atoms $n = 8.58 \times 10^{28} \text{ m}^{-3}$, the driving force of the transformation $\Delta g = g_{\gamma\gamma} - g_{\alpha\alpha} = 0.00365 k_B T^2 - 10.3952 k_B T + k_B 7191.1424 \text{ J}$. Here k_B is the Boltzmann constant.

The surface areas S_α , S_γ , S'_γ , S'_α , $S_{\alpha\gamma}$ are taken as temperature independent. In the following $S_{\alpha\gamma}$ is obtained by fixing the size R , the number N_γ , and the corresponding determination of all reasonable radii r of the α - γ interphase surface and direct calculation $S_{\alpha\gamma} = \pi r^2$ (figure 1). Hereby one must distinguish two cases: (i) when the volume of the new phase is smaller than half of the volume of the nanoparticle and (ii) vice versa. The geometry gives: $1/3\pi(R - \sqrt{R^2 - r^2})^2(2R - \sqrt{R^2 - r^2}) = N_\gamma/n$ for case (i) and $4/3\pi R^3 - 1/3\pi(R - \sqrt{R^2 - r^2})^2(2R - \sqrt{R^2 - r^2}) = N_\gamma/n$ for case (ii). The values S'_γ , S'_α are defined by a system of equations taking into account the conservation law $N_\gamma + N_\alpha = N_0$: $S'_\gamma = 2\pi(R^2 - R\sqrt{R^2 - r^2})$ for case (i) and $S'_\gamma = 4\pi R^2 - 2\pi(R^2 - R\sqrt{R^2 - r^2})$ for case (ii).

In this work we shall restrict the discussion in the temperature interval 900–1400 K near the transformation temperature in bulk state $T = 1183$ K. The results of the computations are shown in figure 2. The different curves are drawn at the following conditions: the phase transition is impossible at $T = 1100$ K; the α -to- γ transition may take place at $T = 1160$ K and for higher temperatures. Say, for $T = 1183$ K (transformation temperature in bulk state) the nucleation barrier is about $16.5 k_B T$ at the critical size of the new γ -phase nucleus corresponding to $N_\gamma = 504$ atoms.

Thus, the thermodynamics of phase transformations of nanomaterials deviates considerably from the respective course in the bulk [27–31]. Compared with bulk cases, there exists the possibility of the existence of a metastable phase (for example, at $N_\gamma = 3000$ and $T = 1130$ K in figure 2) instead of the stable one due to a nucleation energy barrier, which could be employed in nanotechnology as a means to improve the physical properties of materials.

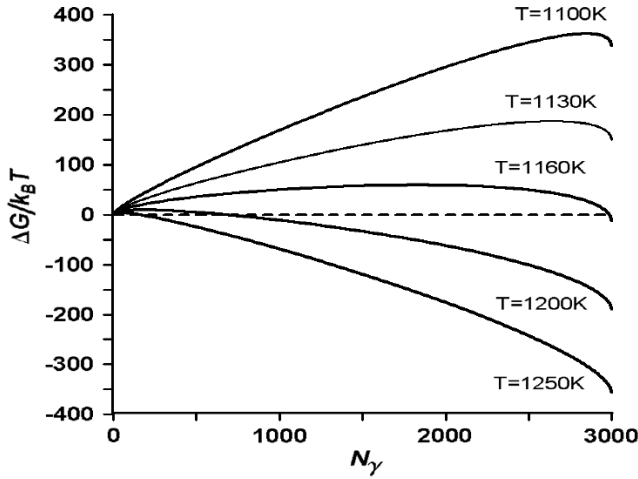


Figure 2. Phase transition energy change versus nucleus size (number of atoms in a γ -Fe) at different fixed temperatures and numbers of atoms in the particle $N_0 = 3000$. The zero point denotes the initial α -phase; the last points of all curves correspond to the γ -phase particle (figure 1).

3. Kinetic model of polymorphic transitions at temperature cycling of a nanopowder

Let us now consider the Fe nanopowder and assume that the nanoparticles are characterized by a monodisperse size distribution. Such an ensemble of nanoparticles is subjected then to heating and cooling. First, we start from low temperatures (figure 1) and increase the temperature with a constant finite rate (heating). Then we stop the temperature change at some point and decrease the temperature (cooling) at the same rate. One cycle refers to a complete change of temperature from some initial value back to the same point (figure 3).

We introduce a size distribution function $f(N_\gamma, t) \equiv f(N_\gamma)$ being equal to the number of new phase nuclei consisting at time t of N_γ atoms. The evolution is described by the kinetic equation of the theory of nucleation–growth processes:

$$\frac{\partial f(N_\gamma)}{\partial t} = f(N_\gamma - 1)v_+(N_\gamma - 1) + f(N_\gamma + 1)v_-(N_\gamma + 1) - f(N_\gamma)\{v_-(N_\gamma) + v_+(N_\gamma)\}. \quad (4)$$

The frequencies of attachment $v_+(N_\gamma)$ and detachment $v_-(N_\gamma)$ of atoms to a new phase cluster of size N_γ are interrelated due to the balance condition: $v_-(N_\gamma) = v_+(N_\gamma) \exp[\frac{\Delta G(N_\gamma) - \Delta G(N_\gamma - 1)}{k_B T}]$. The Gibbs free energy change $\Delta G(N_\gamma)$ may be expressed as a function of time (via the time dependence of temperature). The expression for the frequency $v_+(N_\gamma)$ is obtained by considering the growth of the new γ -phase cluster that has to result from a series of monomolecular additions to the nucleus. The interrelations between $v_+(N_\gamma)$ and $v_-(N_\gamma)$ are essentially much more dependent on the temperature in exponential factors $\Delta G(N_\gamma)/k_B T$ than the one in pre-exponential values. One usually distinguishes so-called diffusion-controlled (bulk) and kinetic-controlled (surface) processes. In the case of nanosized particles the

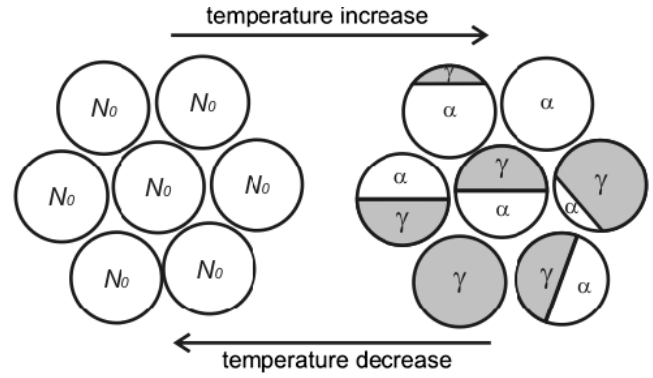


Figure 3. Representation of a polymorphic transition in a nanopowder during temperature cycling: from left to right—ensemble of particles of N_0 size before transformation and the same powder after γ -Fe nucleation. It is assumed that in each nanoparticle only one aggregate of the new phase can be formed.

surfaces have to play the key role. That is why the coefficient of aggregation $v_+(N_\gamma)$ will be taken as that of the kinetic-controlled process [32] and is assumed to be proportional to the probability of molecular additions and the $\alpha - \gamma$ interface area $S_{\alpha\gamma}$, that is to the number of atoms at the interface boundary $N_{\alpha\gamma}$: $v_+(N_\gamma) = DN_{\alpha\gamma}$, $N_{\alpha\gamma} = S_{\alpha\gamma}n^{2/3}$. Hereby the value $n^{-2/3}$ represents the surface area related to one atom. D is an effective diffusion parameter of the material in the vicinity of the $\alpha - \gamma$ interface boundary. In the following, without restricting the main results, D is taken as constant. It can be estimated due to the phonon frequency: $D \sim k_B T/h \approx 10^{13} \text{ s}^{-1}$. Here the temperature is estimated as $T = 1000 \text{ K}$ and h is the Planck constant.

The conservation of the number of particles is included in the following boundary conditions for the size distribution function $f(N_\gamma, t)$ of the new phase:

$$f(N_{\min}, t) = W - \sum_{N_\gamma=N_{\min}+1}^{N_{\max}} f(N_\gamma, t),$$

$$f(N_\gamma, t=0) = \begin{cases} W, & N_\gamma = N_{\min} \\ 0, & N_\gamma \neq N_{\min} \end{cases} \quad (5)$$

$$\frac{\partial f(N_{\max}, t)}{\partial t} = f(N_{\max} - 1, t)v_+(N_{\max} - 1) - f(N_{\max}, t)v_-(N_{\max}),$$

where $N_{\min}$ is the minimal number of atoms in the new phase nuclei, $N_{\max} = N_0$ is the maximal possible number of atoms in each particle, W is the number of particles in the nanopowder.

One can describe the volume fraction ρ of the new phase in the process of temperature cycling with different fixed rates of change of temperature $v = |dT/dt|$ assuming different sizes N_0 of the particles in a powder where the transition occurs:

$$\rho = \frac{\sum_{N_\gamma=N_{\min}}^{N_{\max}} N_\gamma f(N_\gamma, t)}{N_0 W}. \quad (6)$$

If we stop the cycling at some temperature then the system relaxes to the equilibrium state in which some particles will

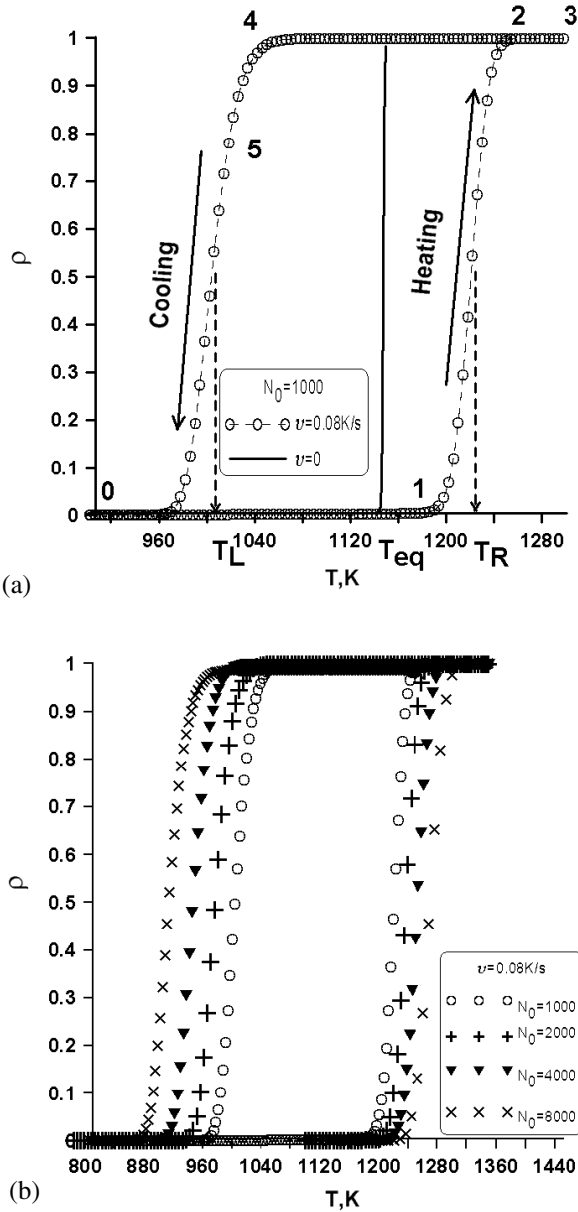


Figure 4. Volume fraction versus temperature for the fixed rate $v = 0.08 \text{ K s}^{-1}$ between 900 and 1300 K: symbol ‘O’ denotes the case $N_0 = 1000$, ‘+’— $N_0 = 2000$, ‘▼’— $N_0 = 4000$, ‘×’— $N_0 = 8000$. The solid curve in (a) is the equilibrium values ρ_{eq} for each fixed temperature and zero rate $v = 0$.

be in single-phase states and the others in two-phase states; the equilibrium size distribution $f_{eq}(N_\gamma)$ and the equilibrium volume fraction ρ_{eq} are reached. The number of particles, $f_{eq}(N_\gamma) \equiv f_{eq}(N_\gamma, T)$, may be found by the Boltzmann distribution in a statistical mechanical sense, so that one can write:

$$\rho_{eq} = \frac{\sum_{N_\gamma=N_{min}}^{N_{max}} N_\gamma f_{eq}(N_\gamma, T)}{N_0 W},$$

$$f_{eq}(N_\gamma, T) = \frac{W}{\sum_{N=N_{min}}^{N_{max}} \exp(-\Delta G(N_\gamma, T)/kT)} \times \exp(-\Delta G(N_\gamma, T)/kT). \quad (7)$$

The constants for numerical simulation are: $D = 2 \times 10^{12} \text{ s}^{-1}$, $N_{min} = 1$, $W = 10^{10}$.

4. Size-dependent hysteresis of $\alpha\text{-Fe} \leftrightarrow \gamma\text{-Fe}$ transformations

The change of the volume fraction ρ of newly formed $\gamma\text{-Fe}$ particles in temperature cycling is presented in figure 4. As one can see in figure 4(a), the temperature cycling 900 K $\leftrightarrow$ 1300 K leads to a loop-like $\rho(t)$ curve. Let us introduce as a simple phase transition criterion in the kinetics of the considered process the condition that the transition is performed when half of the volume is transformed, that is when $\rho = 0.5$ is reached. This criterion determines the value of the temperature of direct transition T_R at the right branch of the hysteresis loop (during heating) and similarly, the temperature of the reverse transition T_L , at the left branch of it (during cooling). The difference $T_R - T_L$ is the width of the hysteresis loop, which is a function of size and the rate v (figure 4(b)). The full curve ρ represents the equilibrium values ρ_{eq} found via equation (7) for each fixed temperature and zero rate $v = 0$. As far as we know, the size-dependent hysteresis loop is observed in the modelling of the kinetics of a heterogeneous transformation of Fe powder here for the first time.

If one also introduces as a statistical phase transition criterion for the equilibrium volume fraction of the new phase, $\rho_{eq} = 0.5$, then one obtains the temperature of this transition, T_{eq} , related to the equilibrium distribution, $f_{eq}(N_\gamma, t)$. Hereby the specific value of the width of the hysteresis loop can be found as $\delta = (T_R - T_L)/T_{eq}$ and presented in the corresponding phase diagram as a function of the sizes and rates v (figure 5).

Statistical generalization of the presented results for different sizes and rates allows one to introduce the notion of a ‘size-dependent superheating limit’ $\delta_R = (T_R - T_{eq})/T_{eq}$ and ‘size-dependent supercooling limit’ $\delta_L = (T_{eq} - T_L)/T_{eq}$. Both values can be defined in a similar way.

It is important that the statistics is characterized by a nearly linear dependence in logarithmic scales, that is:

$$\begin{aligned} \delta &= k(v) \ln(N_0) + a_1(v), \\ \delta_R &= k_R(v) \ln(N_0) + a_R(v), \\ \delta_L &= k_L(v) \ln(N_0) + a_L(v). \end{aligned} \quad (8)$$

Hereby the angles of the slopes of these lines are well defined. Formally, the following conditions must be fulfilled: $k(v) = 0.00442 \ln(v) + 0.0663$, $k_R(v) = 0.00277 \ln(v) + 0.0216$, $k_L(v) = 0.00097 \ln(v) + 0.04389$. It is worth noting that the fitting formulae for slopes are found for the curves δ versus N_0 at the same rate, v . However, due to the fact that the approximations depend on the forth and back temperatures of the phase transition in Fe nanopowder, it has limitations at large rates v and big sizes and is useful for nanometric intervals and small rates, v . Unfortunately, it is not feasible to go to larger sizes or rates due to the fact that for higher temperature intervals $\delta\text{-Fe}$ phase becomes favourable (1665 K for bulk case) and the driving force of the phase transition must be correspondingly redefined.

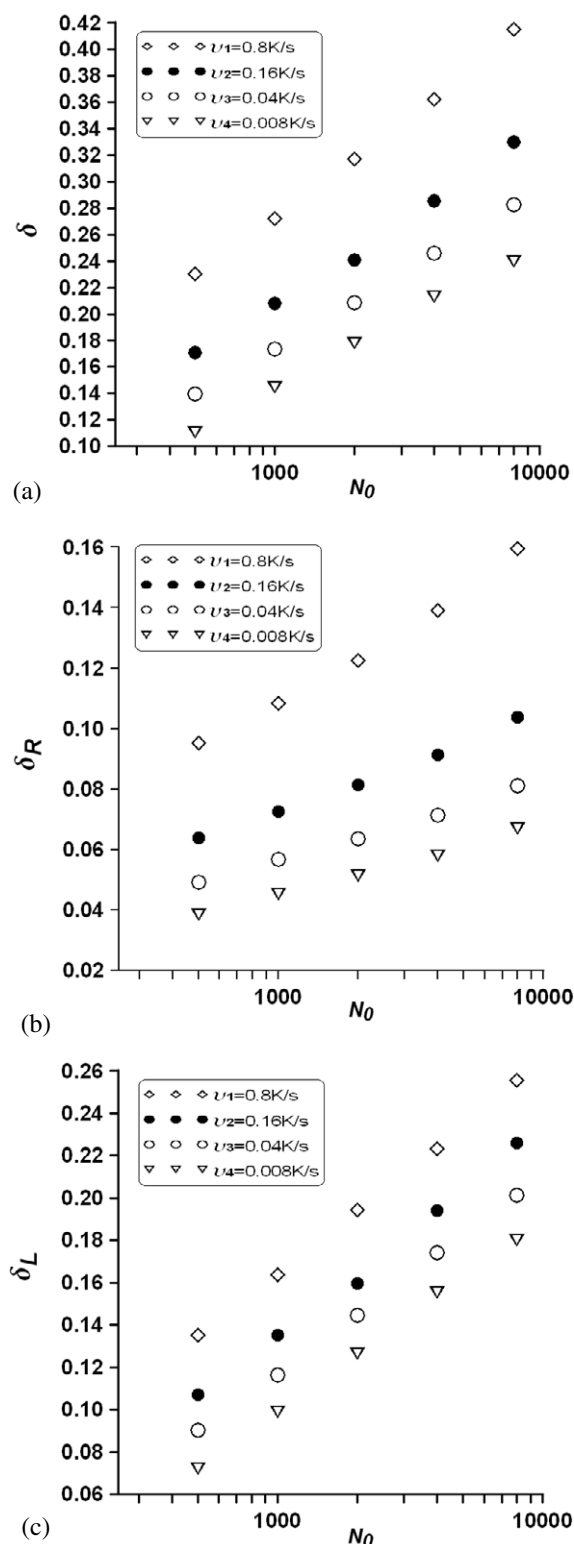


Figure 5. The width of the thermal hysteresis loop versus the size of particles in a nanopowder (a), the size-dependent superheating limit δ_R (b) and the size-dependent supercooling limit δ_L (c) as functions of sizes.

5. Concluding remarks

The theoretical and computer experimental findings of the present paper put new insight into the intensively discussed

topic of size-dependent phase transitions and hysteresis phenomena in nanomaterials. In the present paper a model of polymorphic phase transformations in a Fe nanopowder under temperature cycling is presented. The thermodynamic relations between the energy of transition and the size of nanoparticles were derived theoretically.

For finite rates of temperature changes, ν , one observes size-dependent hysteresis loops. The results of thermodynamic and kinetic approaches show that the size of nanoparticles has a remarkable effect on the kinetics of the transformation. The notions of the ‘size-dependent superheating limit’ and ‘size-dependent supercooling limit’ were introduced and statistically formulated. Statistical averaging results in a linear dependence of the width of the hysteresis loop on the logarithm of the number of atoms in the nanopowder particle.

Finally, we would like to point out that the investigations presented in the paper are devoted to the problem of solid–solid first-order phase transition in nanovolumes. Other intriguing extensions of the present work should involve the cases of (i) melting and solidification of multicomponent metallic nanoparticles and (ii) competitive formation in the nanoparticles of two and/or more phases with different stoichiometries. The mentioned problems based on a similar method will be discussed in forthcoming publications.

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