Nucleation mechanism for reconstructive solid-solid phase transitions via melt mediated nanocluster transformation

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A general nucleation mechanism is proposed and justified thermodynamically and kinetically. The authors apply it to the β-δ phase transformation (PT) in the HMX crystal. It explains the observation of a reconstructive PT very close (0.6 K) to the phase equilibrium temperature, despite the large volume change and interface energy. Nanosize clusters of β phase dissolve in a liquid and transform into δ phase clusters. The liquid completely removes the elastic energy generated by a large volume change. Cluster to cluster PT also drastically reduces the change in interfacial energy. Suggested kinetics for the β-δ PT is in good agreement with experiments. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2403900]

Polymorphism in the organic energetic crystal octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is the source of numerous puzzles which have significantly stimulated the development of the general solid-solid phase transformation (PT) theory.[1–4] We recently observed a paradoxical experimental result:[5,6] the reconstructive β-δ PT in HMX starts at 432.6 K, just above the phase equilibrium temperature θ_e=432 K. The β-δ PT is accompanied by a large volumetric expansion, ε^t=0.08. Thus, the associated energy of internal stresses (g^e=9.072 kJ/mol, see Refs. 1 and 3) is very large and, if unrelaxed, it should increase the PT temperature by $g^e/\Delta s_{\beta\text{-}\delta}$=400 K, where $\Delta s_{\beta\text{-}\delta}$=22.68 J/mol K is the change in molar entropy. The barrier to nucleation due to the interface energy makes an additional, significant increase in the nucleation temperature. No existing theory can explain nucleation so close to θ_e. The above result was obtained for HMX crystals bonded with a binder (Estane and nitroplasticizer), i.e., for the PBX 9501 formulation.

In this letter, we suggest that the liquid medium (nitroplasticizer) contains nanometer size clusters of β phase. HMX is somewhat soluble in the nitroplasticizer and such clusters may appear as a suspension in the liquid subsequent to erosion of the β HMX surface during dissolution and the liberation of surface asperities. If such a cluster undergoes the β-δ PT, the change in interface energy can be small enough (or even negative) to allow nucleation near the phase equilibrium temperature. Such a mechanism also completely removes the energy of elastic stresses. The kinetic equation for nucleation is derived. We combine it with our recent results on the virtual melting (VM) growth mechanism[1–7] to develop a physically based kinetic model for the β-δ PT, which is in very good correspondence with our experiments. This nucleation mechanism can be applicable to various material systems and can be used to control PTs.

Nucleation mechanism. Our preliminary observations[8] led us to a hypothesis that β HMX dissolves in the liquid medium (in nitroplasticizer), and at temperatures above θ_e nucleates the δ phase at the interface between the HMX and the liquid. We initially show that this nucleation mechanism completely removes the huge energy of internal stresses that would appear for direct solid-solid PT. Indeed, if nucleation occurs in a closed liquid cavity with volume V_l, then the elastic energy due to the volume change is 0.5 $K\varepsilon_0^2$, where K is the bulk modulus of the liquid, $\varepsilon_0=\varepsilon^t V_n/V_l$ is the volumetric strain in the liquid, and V_n is the volume of the δ phase nucleus. Taking conservatively the volume of the liquid nitroplasticizer near each HMX crystal $V_l=10^5\times10^5\times10^4=10^{14}$ nm^3 and $V_n=10^3$ nm^3 (see below), we obtain $\varepsilon_0=10^{-11}\varepsilon^t=8\times10^{-13}$ which is negligible (also, volume V_l is not closed in reality). However, as we will show below, the barrier to nucleation due to the interface energy is still too high to allow such a nucleation near the θ_e. The nucleation time for thermally activated nucleation is described by the transition state theory and the Arrhenius equation[9,10]

$$t_n = \tilde{t}\frac{h}{k\theta}\exp\left(\frac{E_n}{k\theta}\right) = \frac{\bar{t}}{\theta}\exp\left(\frac{E_n}{k\theta}\right), \qquad (1)$$

where k and h are Boltzmann's and Planck's constants, E_n is the activation energy for nucleation (equal to the energy of a critical nucleus), and $\bar{t}$ and $\tilde{t}$ are preexponential multipliers. For a spherical nucleus,[9]

$$E_n = \frac{16\pi\Delta\gamma^3 M^2}{3\Delta g_{\beta\text{-}\delta}^2\rho^2}, \qquad (2)$$

where $\Delta g_{\beta\text{-}\delta}=-(\Delta s_{\beta\text{-}\delta}(\theta-\theta_e)-p\Delta v_{\beta\text{-}\delta})$ is the molar change in the Gibbs potential during the β-δ PT, $\Delta\gamma$ is the change in surface energy, ρ=1847 kg/m^3 is the mass density of the parent phase, M=0.296 kg/mol is the molecular mass, p is the pressure, and $\Delta v_{\beta\text{-}\delta}$=1.28$\times10^{-5}$ m^3/mol is the jump in the molar volume.[1,5,6] The change in thermal strain and elastic strains can be neglected in comparison with $\Delta v_{\beta\text{-}\delta}$.[3,7] Substituting all the above data in Eq. (2), we obtain for p=0

$$E_n = \frac{8.366\times10^{-10}\Delta\gamma^3}{(\theta-432)^2}. \qquad (3)$$

Nucleation can realistically occur during the time of an experiment only if $E_n=(40–80)k\theta$.[9] Taking $E_n=80k\theta$ and θ=432.6 K, we obtain an estimate of the change of surface

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energy that would allow the nucleation: $\Delta\gamma < 6 \times 10^{-4}$ J/m^2, which is an extremely small number. For homogeneous nucleation of δ crystals in the molten nitroplasticizer, $\Delta\gamma$ is the interface energy between the solid δ phase and liquid nitroplasticizer, $\gamma_{\delta\text{-}l}$. Usually the solid-liquid interface energy is at least $\gamma_{s\text{-}l} = 10^{-1} - 10^{-2}$ J/m^2, i.e., homogeneous nucleation is impossible (as for most PTs). Assuming $\gamma_{s\text{-}l} = 6 \times 10^{-2}$ J/m^2, then the activation energy for homogeneous nucleation is six orders of magnitude larger than allowable by the equation $E_n = 80k\theta$. Even for $\gamma_{s\text{-}l} = 10^{-2}$ J/m^2, an eventual increase in the driving force for a PT by one order of magnitude, driven either by the eventual change in θ_e, the thermodynamics of dissolution of HMX in the liquid phase, or by an eventual chemical reaction, does not change our conclusion about the impossibility of homogeneous nucleation. For heterogeneous nucleation at the flat surface of the β phase[9] $E_n = 8.366 \times 10^{-10} \gamma_{\delta\text{-}l}^3 S(\alpha)/(\theta-432)^2$, $S(\alpha) := (2 + \cos\alpha)(1-\cos\alpha)^2/4$, where the wetting angle α is determined by the equilibrium of the components of surface tension along the flat interface:[9] $\gamma_{\beta\text{-}l} = \gamma_{\beta\text{-}\delta} + \gamma_{\delta\text{-}l}\cos\alpha$ [i.e., $\cos\alpha = (\gamma_{\beta\text{-}l} - \gamma_{\beta\text{-}\delta})/\gamma_{\delta\text{-}l}$], where $\gamma_{\beta\text{-}\delta}$ is the β-δ interface energy and $\gamma_{\beta\text{-}l}$ is the energy of interfaces between the β phase and surrounding liquid. We cannot expect a low-energy coherent interface between the β and δ phases, because it will cause a significant increase in elastic energy of internal stresses and therefore a thermodynamic barrier for nucleation. For an incoherent interface $\gamma_{\beta\text{-}\delta} \simeq 1$ J/m^2 $\simeq 10\gamma_{s\text{-}l} - 100\gamma_{s\text{-}l}$. Heterogeneous nucleation would be effective for $\cos\alpha \simeq 1$, i.e., for $\gamma_{\beta\text{-}l} \gg \gamma_{\beta\text{-}\delta}$; we have the opposite situation $\gamma_{\beta\text{-}l} \ll \gamma_{\beta\text{-}\delta}$ for which the equilibrium equation $\gamma_{\beta\text{-}l} = \gamma_{\beta\text{-}\delta} + \gamma_{\delta\text{-}l}\cos\alpha$ cannot be fulfilled and wetting is impossible. Thus, heterogeneous nucleation at the surface of the β phase is energetically even less favorable than homogeneous nucleation.

We suggest the following mechanism for the β-δ PT through a liquid medium. We assume that the liquid medium contains nanometer size clusters of β phase which may appear as surface asperities are liberated from the β HMX surface during dissolution into the binder. If such a cluster undergoes the β-δ PT, then the activation energy is determined by Eq. (2) [or Eq. (3)] with $\Delta\gamma = \gamma_{\delta\text{-}l} - \gamma_{\beta\text{-}l}$. Since $\gamma_{\delta\text{-}l}$ and $\gamma_{\beta\text{-}l}$ are of the same order of magnitude, the difference $\gamma_{\delta\text{-}l} - \gamma_{\beta\text{-}l}$ can be much smaller than $\gamma_{\delta\text{-}l}$ (or $\gamma_{\beta\text{-}l}$), i.e., it can be as small as $(4.7-5.9) \times 10^{-4}$ J/m^2 required by the condition $E_n = (40-80)k\theta$,[9] or smaller. Moreover, it can even be negative, i.e., barrierless nucleation of the δ phase may occur in the β cluster. In fact, for one of the PTs, β-δ or δ-β, $\Delta\gamma$ is definitely negative.[9] The size of the cluster can be determined by the equation[9]

$$r_c = \frac{2\Delta\gamma M}{\Delta g_{\beta\text{-}\delta}\rho} = 1.4 \times 10^{-5}\frac{\Delta\gamma}{(\theta-432)}. \qquad (4)$$

For $\theta = 432.6$ and $\Delta\gamma = 4.7 \times 10^{-4}$ J/m^2 (see below), we obtain $r_c = 11$ nm; a decrease in $\Delta\gamma$ and/or increase in θ-432 will reduce the cluster size proportionally.

The most probable place where a critical δ phase cluster may appear is near the interface between the β phase and nitroplasticizer. The nucleus can grow via dissolution of the β phase atoms, their diffusion through nitroplasticizer toward the growing δ crystal, and their crystallization on the surface of the stable δ crystal. The macroscopic growth kinetics will only be affected by those operational nuclei (from the population of supercritical nuclei) which are close to the β phase surface and have the smallest diffusion path. A few δ crystals may touch the β crystal surface (in particular, due to gravitational and/or electrostatic forces) and form a β-δ interface, initially with a very thin layer of nitroplasticizer, then (when interface area grows due to the β-δ PT) without it. Thus, the suggested cluster to cluster PT completely removes the elastic energy of internal stresses and drastically reduces the change in interfacial energy; it allows nucleation very close to θ_e. It will be used below to develop a mechanism-based kinetic model for the β-δ PT.

Transformation kinetics. The VM *growth* mechanism results in the following equation for the β-δ phase interface velocity:[1,3,7] $v = v_0 b/\theta$, where

$$b := Q\frac{k\theta}{h}\exp\left(-\frac{\Delta h_{\delta\text{-}m} + p\Delta v_{\delta\text{-}m}}{R\theta}\right)\left[\exp\left(-\frac{\Delta g_{\beta\text{-}\delta}}{R\theta}\right) - 1\right],$$

v_0 and Q are parameters, R is the universal gas constant, the heat of fusion of the δ phase is $\Delta h_{\delta\text{-}m} = 69.9$ kJ/mol, and the change in molar volume during melting of the δ phase is $\Delta v_{\delta\text{-}m} = 1.05 \times 10^{-5}$ m^3/mol.[5,6] This equation is in good agreement with various experiments under normal pressure.[2,3,7] It was shown in Refs. 3 and 7 that the rate of change of the volume fraction of the δ phase due to growth stage, $\dot{c} \sim v\Sigma$ [where $\Sigma \sim c(1-c)$ is the $\beta-\delta$ interface area], had the form $\dot{c} = bc(1-c)$. In contrast to previous papers,[5–7,11] where formal phenomenological models for *nucleation* were used and the rate of change of the volume fraction due to nucleation and growth were combined additively, here a more physical approach is used. Nucleation is treated using the specific nucleation mechanism and corresponding thermodynamics and kinetics. Nucleation contributes to the overall kinetics through the initial condition for growth: it supplies an operational nucleus of volume fraction c_0 during the time of formation of operational nucleus t_0. Thus, the overall nucleation and growth kinetics equation is

$$\dot{c} = bc(1-c), \quad c(t_0) = c_0. \qquad (5)$$

Since diffusional growth of the critical nucleus to the operational nucleus is related to a number of unknown parameters (rate of dissolution, diffusion coefficient, diffusion path, and rate of crystallization), we assume for simplicity that t_0 is proportional to t_n, i.e., from Eq. (1)

$$t_0 = \frac{\bar{t}_0}{\theta}\exp\left(\frac{E_n}{k\theta}\right) = \frac{\bar{t}_0}{\theta}\exp\left(\frac{6.058 \times 10^{13}\Delta\gamma^3}{(\theta-432)^2\theta}\right). \qquad (6)$$

The solution to Eq. (5) is

$$c = \frac{c_0}{c_0 + (1-c_0)\exp(-b(t-t_0))}. \qquad (7)$$

From the condition $c = 0.5$, one can find the time to half conversion as follows:

$$t_{0.5} = t_0 + \ln((1/c_0) - 1)/b. \qquad (8)$$

The time to reach any volume fraction is the sum of the time for appearance of an operational nucleus t_0 and time for its growth. Substituting into Eq. (8) for $t_{0.5}$, Eq. (6) for t_0, and Eq. (5) for b, we obtain that $t_{0.5}$ depends on three material parameters: $\bar{t}_0$, $\Delta\gamma$, and $\bar{Q} = \ln((1/c_0)-1)/Q$.

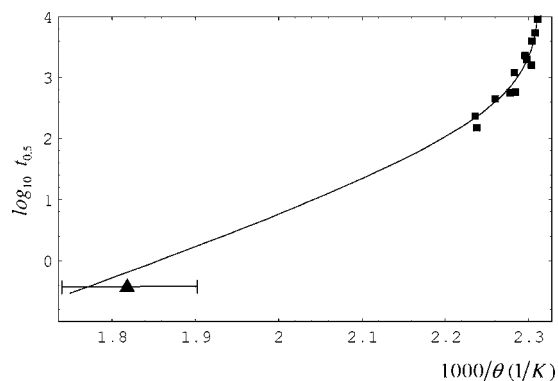In Fig. 1, comparison of the prediction of Eq. (8) with the experimental data on time to half conversion for β-δ PT

FIG. 1. Logarithm of the time to half conversion vs $1000/T(K)$ for β-δ PT in the HMX based explosive PBX 9501. A comparison of the predictions of Eq. (8) (solid line) with experimental data. The squares are data from measurements made by second harmonic generation Refs. 5 and 6 the diamond is the the conversion half time measured during laser heating Ref. 12.

(Ref. 5 and 6) demonstrates good agreement. Parameters $\bar{t}_0$ $=4.5\times10^{-4}$ s, $\Delta\gamma=4.7\times10^{-4}$ J/m^2, and $\bar{Q}=5.822\times10^{12}$ are determined from the best fit to experimental values of $t_{0.5}$. Parameters c_0 and Q can be varied to achieve the best fit of the shape of the $c(t)$ curves. However, we do not need this degree of freedom. We did not change our growth model developed in (Refs. 3 and 7) and retained the value of the scaling parameter, $Q=7\times10^{-13}$, and obtained $c_0=0.016$. Figure 2 demonstrates a very good agreement between our $c(t)$ curves [Eq. (7)] and experiment.

In summary, we suggested a melt mediated nanocluster transformation nucleation mechanism for β-δ PT that allows nucleation near the phase equilibrium temperature. W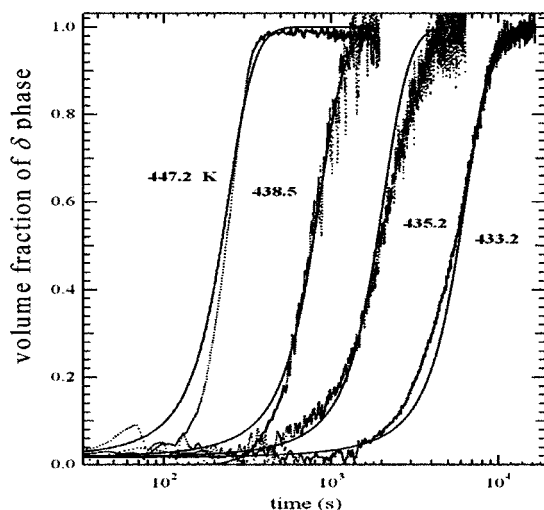e use this nucleation mechanism and our growth mechanism via the VM (Refs. 1–3), to develop physically based equation for the overall kinetics of β-δ PT. The kinetic equation is in good agreement with experiments at ambient pressure. Since it is mechanism based, it can be used for high pressure as well; experimental determination of the kinetic equation at high pressure (and consequently, temperature) is very difficult due to chemical decomposition of HMX and binder and their volatility. At the same time, such a kinetic equation is very important for the modeling of ignition and postignition behavior of HMX as an explosive because of the greater sensitivity and different properties of the δ phase. A similar mechanism may be operative in HMX without a binder as well. Different solvent inclusions remaining in a crystal from the synthesis of HMX could play the role of the liquid or gas media instead of nitroplasticizer.[8] This hypothesis, however, requires further experimental proof and theoretical analysis.

Knowledge of the suggested nucleation mechanism can be used to activate similar mechanisms for other PTs, especially with large volumetric strain and interface energy. This will allow a reduction of the PT pressure and temperature by substituting a direct solid-solid PT by a cluster-cluster PT in a proper liquid or gas media. It will also allow the discovery of phases previously hidden due to large volumetric strain and interface energy which cannot appear by a direct solid-solid PT. For example α HMX is stable at $382.4<\theta$ <430 K; however, β HMX does not transform to α in this temperature range; it transforms to δ at $\theta>432$ K. In the presence of various solvents, α HMX appears at $382.4<\theta$ <430 K.[13] Furthermore, by a proper choice of solvent, one can nucleate and grow the desired metastable phase if the change of interface energy during cluster to cluster PT for this phase is significantly smaller than for the stable phase.

FIG. 2. Comparison between prediction of Eq. (7) (solid curves) with experimental data for β-δ PT in the HMX based explosive PBX 9501 (Refs. 5 and 6) under isothermal conditions. The volume fraction of the δ phase c is equal to the square root of the measured second harmonic generation intensity from the HMX δ phase.

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