Physical mesomechanics and nonequilibrium thermodynamics as a methodological basis for nanomaterials science

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The dependence of the Gibbs thermodynamic potential on the molar volume in external force fields has been analyzed to show that all structural-scale states of a solid can be represented by a scale hierarchy of crystal fragmentation as the degree of nonequilibrium of the material increases. In the hierarchy of scale levels, particular emphasis has been placed on structural ranges: submicrocrystalline ($d > 100$ nm), nanosized ($d = 30$–100 nm) and nanostructural ($d < 30$ nm). Special thermodynamic-nanostructural states that differ in qualitative terms from other structural-phase states of solids are associated with a size range less than 30 nm. The nanostructural states are formed solely in highly nonequilibrium solids as a pre-transition stage where translation invariance of the materials is violated in the vicinity of zero Gibbs thermodynamic potential. A central role of local hydrostatic-tension zones in the fragmentation mechanisms seen at all scale levels is substantiated. It is essential that the Gibbs thermodynamic potential for a nonequilibrium crystal be kept within a range of negative values to provide continuity of the material under loading. The nanostructural state of a highly nonequilibrium solid arises in the regions surrounded by quasi-amorphous interlayers characterized by the Gibbs thermodynamic potential of positive sign. Further increase in the degree of nonequilibrium of the solid causes porosity to develop in the local hydrostatic tension zones. A logical implication of this work is that physical mesomechanics and nonequilibrium thermodynamics form a fundamental methodological basis for nanomaterials science.

Keywords: physical mesomechanics, nonequilibrium thermodynamics, nanomaterials science

1. Introduction

A basic property of a crystal in a stable thermodynamic state is translation invariance determined by the electron energy spectrum of the solid. It is this fundamental characteristic of crystals which underlies the current theory of solids. In external force fields of any origin, the translation invariance of crystal lattice is violated in local regions of solids. The effect is evident as defects of different types such as vacancies and interstitial atoms, atom-vacancy nanoclusters of different configurations, dislocations, disclinations, twins, meso- and macroscale localized shear bands, cracks, etc. All but point defects are associated with local structural or structural-phase transformations that take place in hydrostatic tension zones of different scale [1]. Violation of the translation invariance in a defect crystal causes its internal energy to increase. Because of this, the crystal is being constantly fragmented, and the defects are displaced toward fragment interfaces to form mesoscopic structural-scale levels of plastic deformation. These processes must be accounted for in terms of physical mesomechanics and nonequilibrium thermodynamics.

It is the goal of this work to examine a thermodynamic approach to a description of fragmentation of solids in high-energy fields. Particular attention is given to pre-transition two-phase states that occur in nonequilibrium solids in the case where the Gibbs thermodynamic potential approaches zero. These are nanostructural states in the vicinity of the crystal–amorphous state transformation. We suggest that generation of nanosized structures in solids (for $d > 30$ nm) be regarded as nanostructuring of the materials.

2. The nonequilibrium thermodynamics of fragmentation of solids in external force fields

Metastable mesoscopic substructures of different scales formed in a nonequilibrium crystal under tension give rise to local minima in the plot of the Gibbs thermodynamic potential $F(v)$ against the molar volume v shown in Fig. 1. The structures should be described in terms of the thermo-

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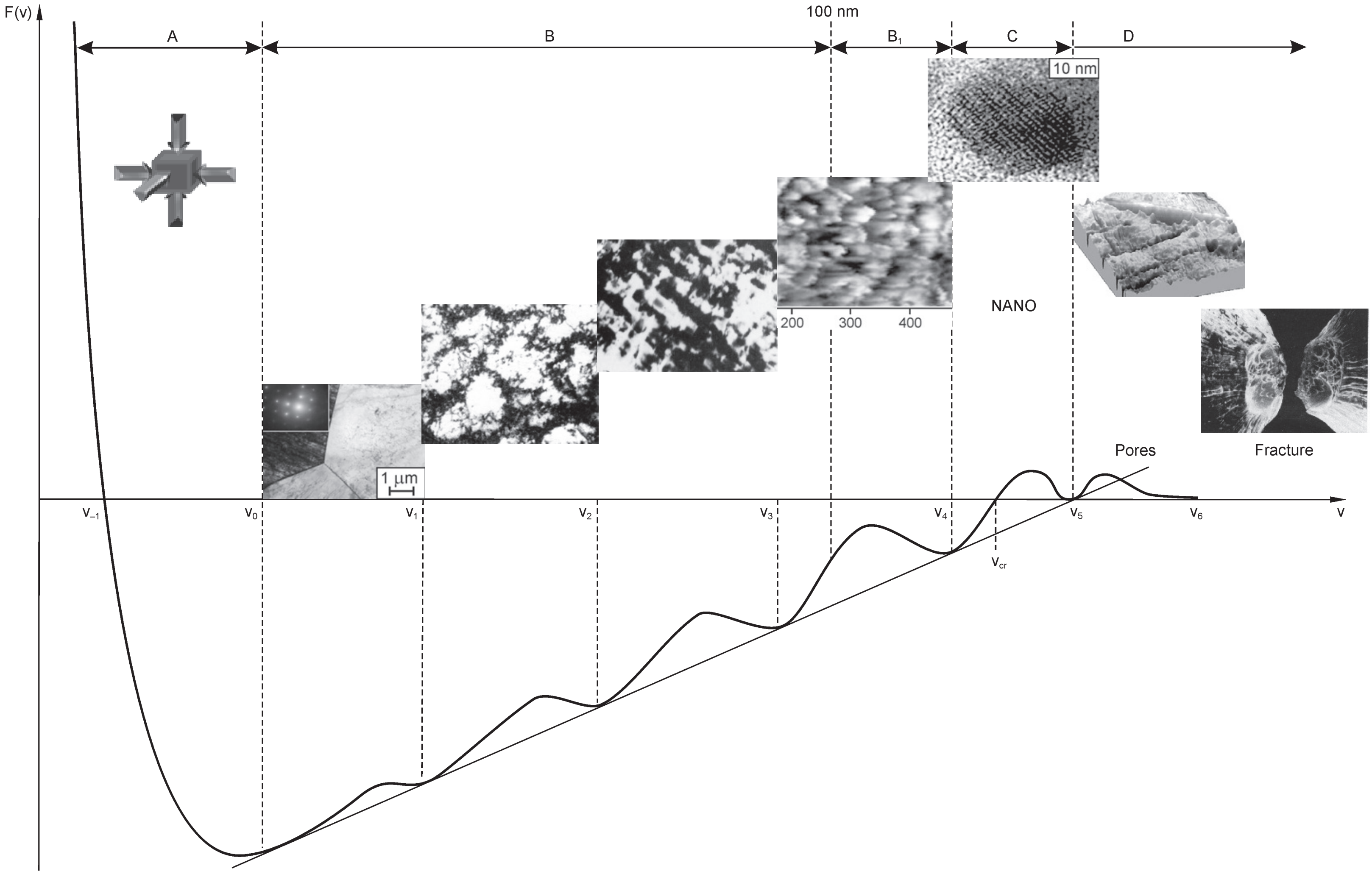

Fig. 1. Gibbs thermodynamic potential F versus molar volume v with allowance made for local hydrostatic tension zones of varying scale where defect structures are generated: hydrostatic compression (A), mesoscopic substructures of different structural-scale levels (B), nanosized structures (B_1), nanostructural states (C) and porosity and fracture (D)