INFLUENCE OF SPATIAL HETEROGENEITY ON (NANO)CRYSTALLIZATION OF RAPIDLY QUENCHED IRON AND COBALT BASED SYSTEMS

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Micromechanisms and energetics of transitions from metastable to more stable sta-te were investigated in complex metastable disordered systems prepared by rapid quenching from the melt from the viewpoint of spatially (structurally) correlated distribution of transfor-mation rates of individual microprocesses controlling the transition process. Using a novel, model-independent method for determination of continuous distributions of process rates it was possible to obtain information on distributions of true activation energies of these micro-processes. Detailed analysis of subdistributions of microprocesses active at each stage a of transition yielded also the information on temperature dependence of the activation energies. We have analyzed different nanocrystal-forming iron and cobalt based systems. New information was obtained with respect to the original local ordering of atoms in the amorphous state and its influence on the formation of nanostructures. Additional information was extracted which allowed to compare processes in the early stages of nanocrystallization with those activated at the end of this transformation. The origin of distributions of microprocess rates or, alternatively, of activation energies, i. e. dynamically heterogeneous behaviour, is discussed and correlated with the expected clustered structure of the amorphous state, i. e. spatial heterogeneities having distinct ordering within the disordered matrix.

1. Introduction

The concept of heterogeneity in complex disordered metastable systems is quite broad, involving structures and phenomena in systems of different origin such as high molecular weight liquids, polymers, undercooled liquids or melts and metallic glasses. The interest in metallic glasses lies in the fact, that they represent systems with strongly interacting constituents (metal-metal, metal-metalloid) and provide possibility to investigate phase transitions from amorphous or undercooled states in the vicinity of the glass transitions. Furthermore, they are systems where, as a paradox, atomic disorder exists along with a certain specific degree of local ordering (clusters, polyatomic aggregates, etc.). From the viewpoint of dynamics, transitions in metallic glasses are typically nonexponential on time and temperature scales, especially in a wider interval of these variables, a phenomenon observed in true dynamic relaxations (after a suitable excitation), in structural relaxations with preservation of the amorphous state as well as in phase transitions from amorphous to a more stable state. It is of principal interest to verify the correlation between such dynamically heterogeneous behavior and microstructural heterogeneities in amorphous structure manifested through specific micromechanisms controlling the transition thermodynamics.

2. Spatial versus dynamic heterogeneity in complex disordered systems

Time or temperature dependence of a convenient physical property or quantity $P(t,T)$ is needed to determine the dynamics of generalized "relaxation" processes, especially the rates of the microprocesses controlling these "relaxations", as described by the Kohlrausch-Williams-Watts

(KWW) equation in the form $P(t,T)=P_0 \exp[-(t.\lambda)^{\text{ß}}]$, where $\lambda = \lambda_0 \exp(-E_a/RT)$ is the microprocess rate in classical Arrhenius form with the corresponding constant activation energy E_a and constant preexponential (or frequency) factor λ_0. In simple processes a single rate λ is observed and the value of the extrinsic KWW exponent $\text{ß}=\text{ß}_{ex}=1$. In more complex systems a deviations from this behavior on macroscopic scales is represented by a deviation of ß from unity. A more exact treatment is by using several discrete microscopic rates with specific weights P_{i0} as

$$P(t) \sim \sum_{i=1}^{\infty} P_{i0} \exp[-(t.\lambda_i)^{\beta}] \tag{1}$$

or a continuous distribution of process rates (probability density function) pdf(λ) as

$$P(t) \sim \int_0^{\infty} pdf(\lambda) \exp[-(t.\lambda)^{\beta}] d\lambda. \tag{2}$$

This approach is valid strictly only for parallel processes running independently of each other, i. e. where each degree of freedom or spatial region "relaxes" independently with its own λ. Under certain, not very limiting assumptions, however, it may be applied to processes on the path to equilibrium through series of serial (sequential) processes as well. The distribution of processes reflected through their rate distribution pdf(λ) should have direct correlation with microscopic sources of such distributions - with intrinsic microstructural heterogeneities.

Of all questions concerning structural heterogeneities in complex metastable amor-phous systems such as their size, lifetime and dynamics, the question about their spatial and thermodynamic origin is the most important one. One of the sources of spatial heterogeneities lies in the nature of the formation of amorphous rapidly quenched systems due to the thermo-dynamics of rapid quenching of strongly interacting polycomponent melts; the process itself can create a distribution of initial thermodynamic states in the amorphous system and thus a distribution of activation energies for the same type of "relaxation" process. Such qualitative picture shown in Fig. 1, is termed as "potential energy landscape" [1]. Another natural source of distributions is thermodynamically stable dynamic distribution of embryos in any under-cooled liquid, melt or amorphous solid close to glass transition with homogeneous nucleation.

Dynamics of transition to a more stable state can be studied by the analysis of isother-mal time evolution of transformed volume fraction x(t) using either a simple Avrami equation $x(t)=1-\exp[-(t\lambda)^n]$, where n is the Avrami parameter, for (rare) simple cases with single pro-cess rate λ or using an Avrami-like analogue of the KWW equation (2) for complex systems.

$$x(t) = 1 - \int_0^{\infty} pdf(\lambda) \exp[-(t.\lambda)^n] d\lambda. \tag{3}$$
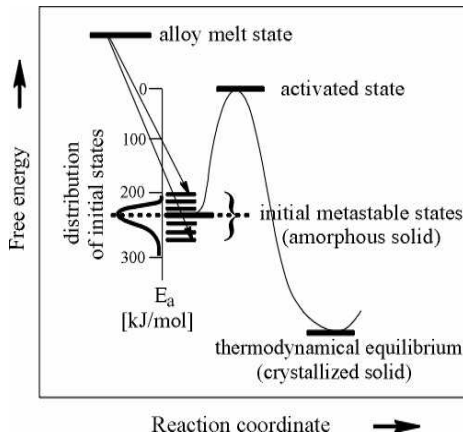

Fig. 1. Distribution of initial energetic states (potential energy landscape) leading to the distribution of activation energies controlling transition from amorphous state.
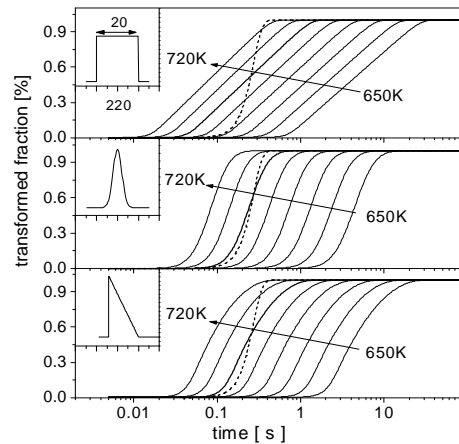
Fig. 2. Transformed volume fractions x(t) for the three activation energy distribu-tions (in insets) compared with x(t) for sin-gle-rate transformation at 700K (thick and dashed lines, respectively) with the same mean Ea and $\lambda_0=10^{16}s^{-1}$; the Avrami n=4.

The importance of even a very narrow distribution of activation energies E_a for the "relaxation" dynamics and especially for its heterogeneous behavior is shown in the following consideration. Let us assume a distribution of activation energies pdf(E) normalized to unity around a mean arbitrary value of 220 kJ/mol commonly observed for transformations in metallic glasses. In relaxation processes a box-like distribution of ±10 kJ/mole is plausible. Fully disordered systems may be expected to have a Gaussian distribution; let its width in half-maximum be 7 kJ/mol. The last case with triangular distribution decreasing from ~214 to 230 kJ/mol may be considered a reasonable approximation for nucleation and growth processes. In all three cases shown as insets in Fig. 2 the value of E_a~220 kJ/mol ± 5%, far below the accuracy of most experimental methods. Assuming transformation kinetics given by the relation (3) for complex processes with rate distributions pdf(λ)=pdf(E_a)/RT [2], the transformed volume fractions x(t) in the temperature range from 650 to 720K are shown in Fig. 2. The box distribution yields x(t) with linear part in log t ranging over several decades on the time scale, much wider than that for simple Avrami relation with only a single mean transformation rate λ (dashed line for 700K) and very similar to the usually observed structure relaxation behavior. The Gaussian and triangular distributions lead to narrower, yet still quite broad x(t) with specific smooth behavior both at the onset and at the end of the process. In all cases the presence of the distributions leads to pronounced deviations from the simple single-rate transformation behavior. However, even such model manifestation of dynamic heterogeneity, cannot be analyzed, either qualitatively or quantitatively, by the classical kinetic analysis methods which provide single values of kinetic parameters only.

3. Transition from amorphous state - continuous distribution analysis with temperature-dependent activation energies

In real transformation processes temperature dependence of activation energy of pro-cess rates can be expected. While in simple processes involving single atoms only (diffusion) the effective activation energy is a constant, in processes controlled by viscous flow where cooperative motion of larger number of (clustered) atoms takes place, the activation energy decreases with temperature; in nucleation-controlled processes the activation energy increases with temperature [3]. Furthermore, activation energy of crystallization from amorphous or undercooled states ought to be considered as a weighted sum of activation energies of nucleation and of growth, $E(T)=n_n.E_n(T)+n_g.E_g(T)$, where $n_n.+n_g=n$.

In a selected interval of annealing temperatures the general E(T) dependence may be approximated by a straight line as $E(T)\sim E_0+E'(T-T_0)$ where $E'=dE(T)/dT$ and $E_0=E(T_0)$ at a mean annealing temperature T_0. Then the correct form for microprocess rates can be written as $\lambda(T) = \lambda_{00}$ exp$[-E(T)/RT]$, where λ_{00} is now the true constant preexponential factor. It can be shown easily that $\lambda_{00}= \lambda_0-E'/RT_0$ and $E_a=E_0-E'T_0$. It is obvious that important new information may be obtained from the sign and magnitude of E'(E) and from distributions of activation energies pdf(E(T)) controlling transformation.

Suitable coupling function correlating the evolution of P(t,T) with the transformed volume x(t,T) and fulfilling the necessary and sufficient conditions for such function [3] allows to investigate crystallization from amorphous state in a wide interval of temperatures and to obtain the information suggested above. This can be performed through the K-S approach presented in [2] by solving the set of transformation isotherms (3) as ill-posed problem to obtain rate distributions by means of deconvolution and inverse Laplace transform which allows also to eliminate the effect of experimental noise and instrument resolution function. By constructing a matrix of suitably selected times (corresponding to chosen fraction of transformed volume) for different temperatures it is possible to determine subdistributions of rates of processes active at these times. The moment analysis is applied to these rate subdistributions to yield the activation energy distributions as well as the dependencies of the preexponential factor λ_{00} and temperature coefficient of activation energy E' are obtained as functions of E_0. Simple recalculation yields the values of pdf(E(T)) at arbitrary T and thus allows to predict kinetic behavior.

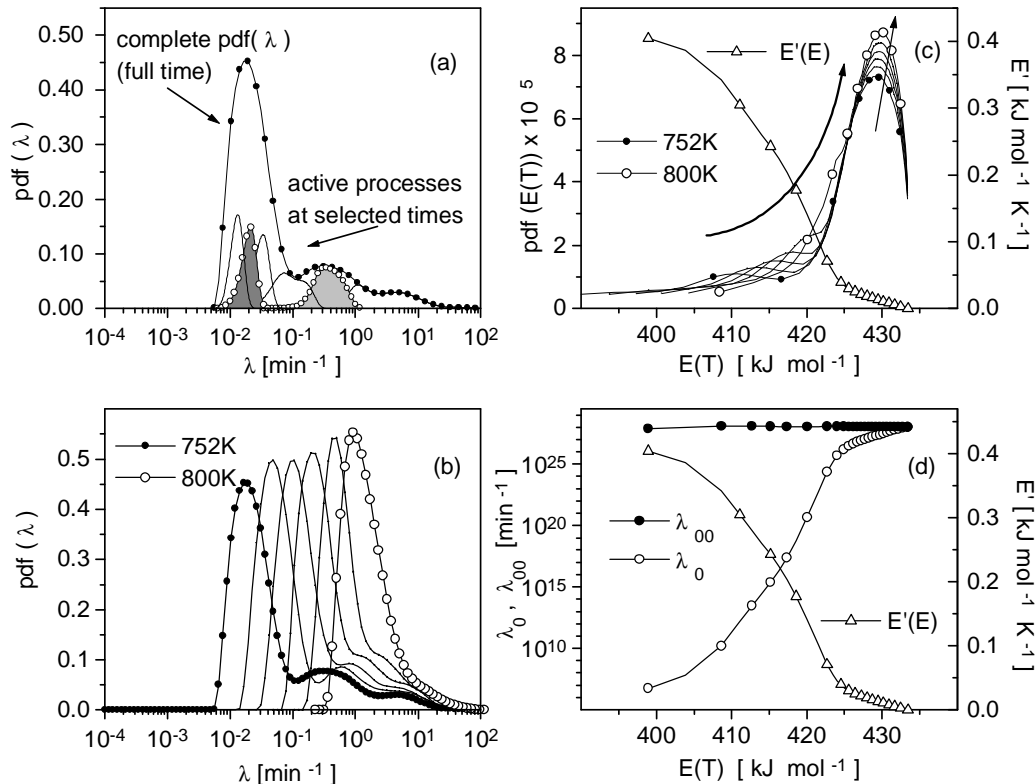Fig. 3. Subdistribution of active processes in rate representation (a), microprocess rate and activation energy distributions pdf(λ) and pdf(E) at different temperatures (b), (c), E' and preexponential factors λ_0 and λ_{00} for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ (Finemet) alloy (d).

4. Energetics of (nano)crystallization and correlation with structural heterogeneity

The outlined approach has been applied to identify and correlate the effect of cluster structure with the microprocesses controlling nanocrystallization in three rapidly-quenched nanocrystal forming systems. The results were obtained from isothermal time dependencies of electrical resistivities in a wide time and temperature range and checked for validity by direct observation using quantitative transmission electron microscopy analysis.

The Finemet alloy in amorphous state is supposed to contain clusters of the Fe-Si and Fe-Nb-B type [4]; upon crystallization ~10-12 nm sized grains of bcc-Fe(Si) are formed. Prior to crystallization by transformation of entire Fe-Si clusters a process of Cu-clustering into fcc-Cu(Fe,Si) was observed. Grain sizes increase very gradually up to ~15 nm with prolonged annealing by diffusion of single Fe atoms from the remaining amorphous matrix. These microprocesses are clearly identified on the dependencies pdf(E) and E'(E) shown in Fig. 3. Copper clustering by nucleation-like processes exhibits high positive value of E' with the corresponding pronounced shifts of pdf(E) to higher E with increasing temperature. Nanocrystallization is characterized by lower E' decreasing to zero for the process of nanograin growth involving single Fe atoms.

The Fe-Zr-B and Fe-Cu-Zr-B alloys (Nanoperm, Fig. 4) also form grains of ~10 nm of pure bcc-Fe. Amorphous structure where the existence of Fe clusters poor in Zr and rich in Zr and B was assumed [5] exhibits also the presence of a certain degree of medium-range order (MRO) of about ~1-2 nm. Formation of small Cu clusters was observed in the final stages of nanocrystallization. Negative value of E' (Fig. 4c) can be explained by low degree of rearrangement of Fe atoms in the MRO-Fe clusters needed for nanograin nucleation and thus by low contribution of nucleation to the overall

activation energy which becomes dominated by the part corresponding to growth with viscous flow behavior and thus with E'<0. The value E' attains zero when most of the Zr-poor clusters are used up by the Fe-nanocrystals, leaving only single-atom processes. The crystallization then proceeds slowly by involvement of Fe-Zr rich regions with E' again negative. In Fe-Cu-Zr-B this process overlaps with the Cu clustering, which is a process involving higher degree of rearrangement with nucleation-like behavior and E'>0 (Fig. 4d).
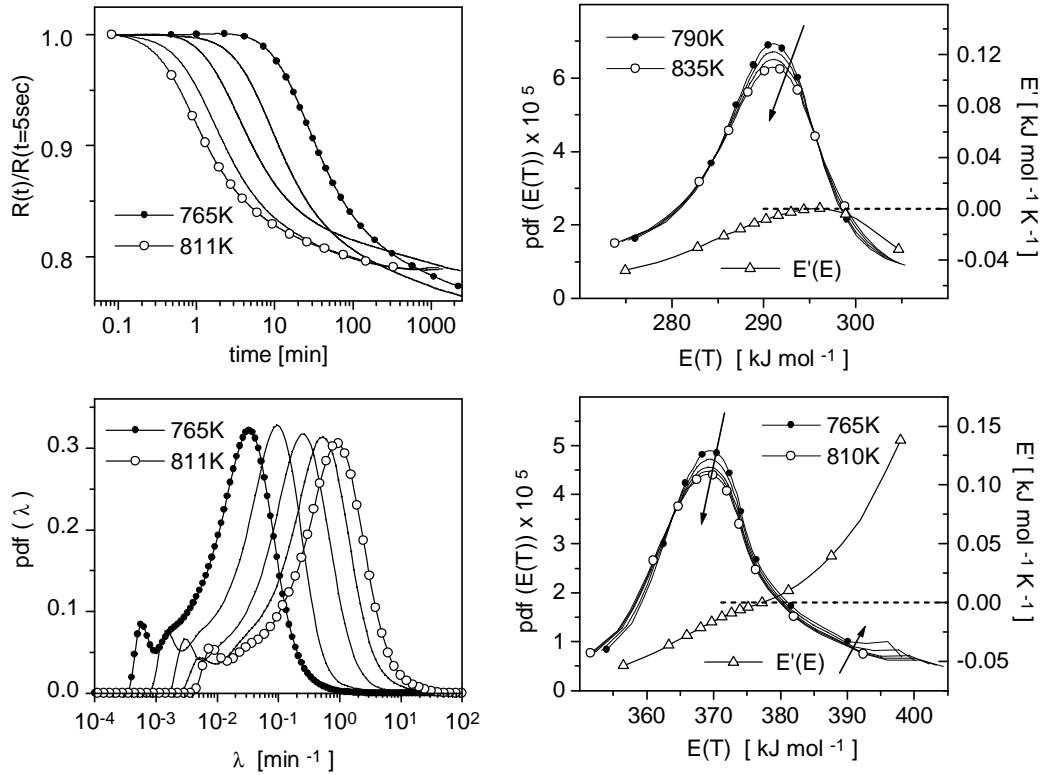

Fig. 4. Isothermal electrical resistivity R(t), microprocess rate distribution pdf(λ), activation energy distributions pdf(E) and temperature coefficient of activation energies E' for $Fe_{87}Zr_7B_6$ and activation energy distributions pdf(E) and temperature coefficient of activation energies E' for $Fe_{86}Cu_1Zr_7B_6$ alloys (Nanoperm).

The Fe-Co-Zr-B alloy (Hitperm, Fig. 5) in amorphous state contains clusters of Fe-Co poor in Zr which are involved in nanocrystallization of disordered bcc-(Fe-Co) and clusters of Fe-Co rich in Zr and B again [6]. The E' dependence (Fig. 5c) is positive and decreasing, indicating that regions with low Zr content require larger degree of nucleation-like rearrangement due to the presence of atoms of Fe and Co in structurally and chemically disordered form with short-range ordering probably dissimilar to the nanocrystalline bcc-(Fe-Co) formed first. After depletion of amorphous matrix from such regions, leaving only single-atom growth processes, E' falls to zero and increases only after activation of processes involving more stable clusters of Fe-Co rich in Zr and B.

In all cases transformation exhibited nucleation and growth character with strict n=4 and very constant values of the preexponential factors λ_{00} (compared to variations of the values of λ_0 over several decades (Figs. 3d, 5d). This indicates the same type of micromechanism active in transformation, yet involving different types of heterogeneities (clusters) present in the amorphous structure formed by rapid quenching of the melt.
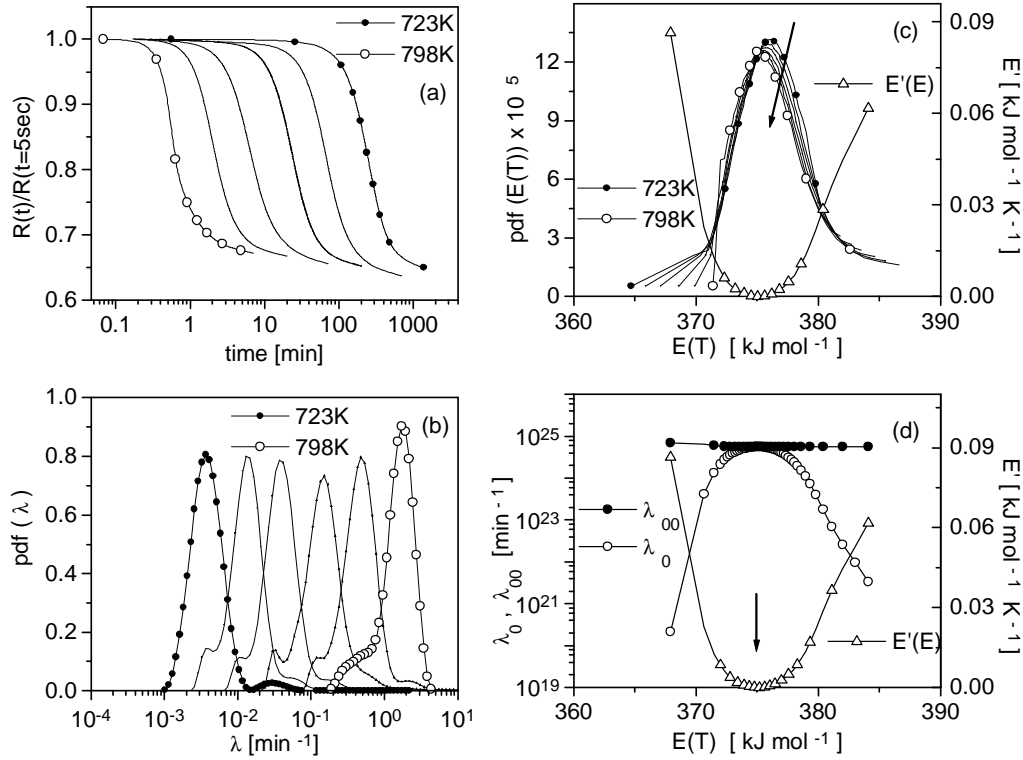
Fig. 5. Isothermal electrical resistivity R(t), microprocess rate and activation energy distributions pdf(λ) and pdf(E), temperature coefficient of activation energies E' and preexponential factors λ_0 and λ_{00} for $Fe_{44.5}Co_{44.5}Zr_7B_4$ (Hitperm) alloy.

5. Discussion: grain size distribution and crystallinity content

One of typical features in (nano)crystallization from amorphous rapidly-quenched state is the presence of two crystallization reactions where the first one involves mainly one type of clusters and covers ~50 vol.% of the entire volume, presumably by incorporation of entire clusters and without need for their breakup or long-range diffusion. A simple simulation of disordered solid with random homogeneous nucleation and spherical growth (n = 4) was performed; grain growth was ceased for grains coming into contact with another grain. The transformation curve was found to behave as $x(t) \sim t^4$ for the initial stages (Fig. 6a). For later stages, however, a sharp deviation from the theoretical Avrami behaviour $x(t) = 1-\exp[-(t.\lambda)^4]$ was observed (Fig. 6b). The transformed volume in simulated transformation attained ~50 vol.% only after very long times and the values of the apparent Avrami parameter decreased from ideal n = 4 sharply to almost zero (similar as in experimental observations). These effects are due to the fact that although the number of all grains present increases linearly with time, the number of grains still growing decreases due to the impingement effect. Thus the grain size distributions (Fig. 6c) for early crystallization stages differ radically from those for later stages, where practically no larger grains are growing any more and a high number of very small grains is observed. The reason for this phenomenon lies in the fact that only small-sized volumes for nucleation are available which, however, make up ~50% of the entire remaining "amorphous" volume. This is again in agreement with experimental observations, e. g. in Finemet after nanocrystallization (Fig. 6d). While the main contribution to the overall crystallinity, which is typically about half of the entire volume, comes from 10-12 nm grains, the presence of large number of very small grains can be observed.
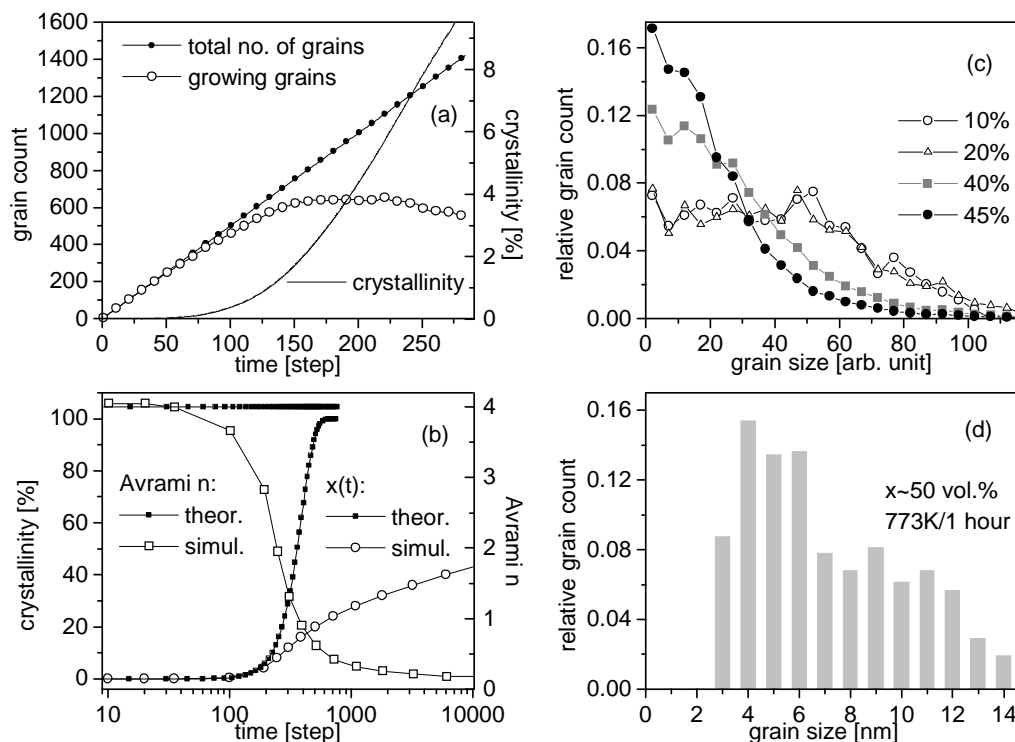
Fig. 6. Time evolution of total and growing grain count and crystallinity for early stages of simulated transformation process (a); comparison of simulated and theoretical time evolution of crystallinity together with the behavior of the Avrami parameter n (b); grain size distribution for different contents of crystallinity (c) and experimental grain size distribution in Finemet alloy after nanocrystallization (d).

6. Conclusions

Kinetic behavior of transformations from amorphous state reflects the activation energy distributions and the evolution of the temperature dependence of the activation energy. The information about the sign and magnitude of the temperature coefficient of activation energy E' contributes to identification of micromechanisms controlling the process of (nano)crystallization. Combined with microstructural observations they suggest a general conclusion about unambiguous correlation between spatial and dynamic heterogeneities which result from the cluster structure of amorphous state and are manifest through system-specific microprocesses involving entire spectrum of cluster entities present in the amorphous structure and ranging from clusters to single atoms.

Acknowledgement

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