Phase field crystal modelling of the order-to-disordered atomistic structure transition of metallic glasses

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Abstract. Bulk metallic glass composites are a new class of metallic alloy systems that have very high tensile strength, ductility and fracture toughness. This unique combination of mechanical properties is largely determined by the presence of crystalline phases uniformly distributed within the glassy matrix. However, there have been very limited reports on how the crystalline phases are nucleated in the super-cooled liquid and their growth dynamics, especially lack of information on the order-to-disordered atomistic structure transition across the crystalline-amorphous interface. In this paper, we use phase field crystal (PFC) method to study the nucleation and growth of the crystalline phases and the glass formation of the super-cooled liquid of a binary alloy. The study is focused on understanding the order-to-disordered transition of atomistic configuration across the interface between the crystalline phases and amorphous matrix of different chemical compositions at different thermal conditions. The capability of using PFC to simulate the order-to-disorder atomistic transition in the bulk material or across the interface is discussed in details.

1. Introduction
Bulk metallic glasses have attracted great attention because of their unique combination of mechanical and functional properties, such as very high strength, large elastic strain limit, exceptional corrosion and wear resistance capability \[1\]. However their very low ductility prevents them from being used as structural materials in wide industrial applications. Recently, a new class of alloy systems, i.e. bulk metallic glass composites (BMGC) has been developed. In these BMGC, the alloy composition is designed to allow ductile crystalline phase nucleate and grow in-situ inside the glassy matrix during solidification. By tailoring alloy compositions and controlling the thermal conditions during solidification, the volume fraction, morphology and size of the crystalline phases can be manipulated to provide a good combination of strength and ductility. However, the fundamental understanding on how the crystalline phases are nucleated in the super-cooled alloy matrix and their growth dynamics is still not fully understood, especially the order-to-disordered atomistic structure transition across the crystalline-amorphous interface.

A number of theoretical analyses have been made in the past to understand the fundamentals of order-to-disordered structure transition in glassy materials. For example, in the condense physics community, mode coupling theory and molecular dynamics have provided insight into the initial stage of atom slowing down in a supercooled liquid due to the increase of viscosity. The dynamic density function theory (DDFT) method \[2-4\] with a conserved form of equation of motion has also been proved to be a useful modeling method to resolve the order-to-disorder transition in glass formation \[5,
6]. However, as explained by Jaatinen [7], the difficulty of DDFT in resolving the sharp peaks in density field causes serious problems in numerical computing. Therefore current research in physics and materials science communities is aiming to develop a general modeling framework to understand and describe glass transition.

Elder, et al [8, 9] firstly proposed the phase field crystal (PFC) methodology in 2002. Since then, extensive research and model development have been made in physics and materials science communities concerning PFC, and recently, dynamic density functional theory and thermodynamic concepts have been also linked to PFC to extend the modelling framework. PFC model operates at atomic length scale (from nm to µm) and diffusive time scales (in µs range), and is a computationally efficient alternative to molecular dynamics simulation methods. Berry [10, 11] argued that PFC is a promising modelling method for the studies of glass transition and crystallization in super-cooled liquid. In this study, we used PFC model to study the atomistic order-to-disordered transition of a binary glass at different thermal conditions, providing more quantitative insight on understanding the order-to-disordered transition across the crystalline and amorphous interface.

2. Phase field crystal model
We used the conserved form of motion equation of a binary alloy PFC model first proposed by Elder, et al [9], and the modified highly nonlinear free energy functional from the Vacancy Phase Field Crystal model (VPFC) proposed by Chan et al [12] in our research. The dimensionless free energy functional of a binary alloy is:

$$F = \int d\vec{r} [f_{AA} + f_{BB} + f_{AB}]$$

where $f_i$ and $f_{AB}$ is the free energy density function, from VPFC [12], a specific form of the free energy function is adopted as below:

$$f_i = \frac{n_i}{2} \left[ r_i + (q_i^2 + \nabla^2)^2 \right] n_i - \frac{w_i}{3} n_i^3 + \frac{u_i}{4} n_i^4 + H_i \left[ |n_i|^3 - n_i^3 \right]$$

and

$$f_{AB} = \frac{n_A}{2} \left( q_{AB}^2 + \nabla^2 \right) n_B + \frac{r_{AB}}{2} n_A n_B$$

where $f_i$ is the free energy density for atom $i$, and $f_{AB}$ is the free energy density for A and B atom mixture. $n_i$ is the scaled time averaged number density of $i$ atom, $r_i$ is related to the liquid modulus, $q_i$ sets the equilibrium distance between atoms of the same species, $q_{AB}$ sets that between A and B, and $H_i$ and $r_{AB}$ are constants. The terms multiplied by $H_i$ penalize $n_i$ when $n_i < 0$, and are the unique feature of the VPFC model. $w_i$ and $u_i$ are derived from the nonlinear terms of DDFT free energy functional [9].

The conserved equation of motion, the so-called model B [13] is adopted to describe the dynamics of the density fields, diffusive relaxations can be described through a direct minimization of the local free energy, and all dynamic processes on shorter time scales can be absorbed into a stochastic noise term, given by

$$\frac{\delta n_i}{\delta t} = \nabla^2 \frac{\delta F}{\delta n_i} + A \xi$$

where, $\xi$ is the conserved noise satisfying the fluctuation-dissipation theorems:

$$\langle \xi(x_1,\vec{r}_1) \xi(x_2,\vec{r}_2) \rangle = \eta \nabla^2 \delta(x_1 - x_2) \delta(\vec{r}_1 - \vec{r}_2)$$
We can rewrite the equation as
\[
\frac{\partial n_i}{\partial t} = \nabla \cdot \frac{\delta F}{\partial n_i} + A \nabla \eta
\] (5)
where \(\eta\) is a n-D vector whose components are independent Gaussian white noise, which can be computed by the Box-Muller transformation, and \(A\) is the amplitude of stochastic thermal noise, which can be considered as temperature [11] in the simulation.

3. Numerical methods
In equation (5), there are several high-order, even-powered gradient terms, making the implicit Euler numerical method more difficult to be derived for the gradients terms. We therefore adopted the semi-implicit pseudo-spectral method (PSM) [13-15] to solve equation (5). Using PSM, all the even-powered gradient terms are converted into even-powered algebraic expressions of the wave vector in the frequency space. PSM is particularly powerful for solving equations that exhibit periodic solutions such as those in this PFC model. After Applying Fourier transformation on both sides of equation (5), and using the forward finite difference method for the time marching, the PSM discretion of equation (5) without the thermal noise term can be written as:
\[
\hat{\nabla}^{\hat{\nabla}} \hat{n}_{i,j} = \Delta k^2 C_{AA} \hat{n}_{i,j}^{\hat{n}_{i,j}} + r_{AB} \hat{n}_{i,j}^{\hat{n}_{i,j}} + \Delta k^2 N(\hat{n}_{i,j}) + \frac{1}{2} \Delta k^2 C_{AB} \hat{n}_{i,j}^{\hat{n}_{i,j}}
\] (6)
where \(C_{ii} = r_i + (q_i^2 + \Delta k^2)^2\), \(C_{AB} = d_{AB}^2 + \Delta k^2\), \(\Delta k^2\) is the discrete Fourier space representation of the \(\nabla^2\) for a finite size system, and \(N(\hat{n}_{i,j}) = -w_i \hat{n}_{i,j}^2 + u_i \hat{n}_{i,j}^3 + 3H_i (\hat{n}_{i,j}^4 - \hat{n}_{i,j}) \hat{n}_{i,j}\). In addition, the thermal stochastic noise term can be discretised as:
\[
\hat{\nabla} \hat{n}_{i,j} = \sum_{i_1 \neq i_2} \left( \frac{\eta_{i_1,i_2} + 2\eta_{i_1,i_2} - \eta_{i_1,i_2} - \eta_{i_1,i_2} - 2\eta_{i_1,i_2} + \eta_{i_1,i_2}}{8\Delta x} \right)
\] (7)
where, \(i, j\) denote the grid indices in the computational domain and \(\Delta x\) is the spatial step size. Because there is no data exchange required between the current one and adjacent grids, we used parallel computing technique to solve the discretised equation (6). The Message Passing Interface (MPI) [16, 17] parallel computing has been implemented together with PSM method.

4. Results and discussion
A series of simulations have been conducted to study the atomistic order-to-disordered transition. All simulations were carried out using a 64-core computing server (Dell PowerEdge C6145) available in our research group. Unless specified otherwise, all parameters defined in the model are referenced from [18] as: \(n_A=0.15\), \(n_B=0.15\), \(q_A=0.9\), \(q_B=0.9\), \(q_{AB}=0.9\), \(r_A=-0.9\), \(r_B=-0.9\), \(H_A=1500\), \(H_B=1500\), \(u_A=1\), \(u_B=1\), \(w_A=0\), \(w_B=0\), \(dt=0.001\), \(dx=\pi/4\), \(N_x=256\), \(N_y=256\).

Since the PFC free energy is derived through Ryoichi Yamamoto functional [19], a representative of DFT functional in solidification. All the parameters entering the PFC model is temperature dependent. However the stochastic thermal noise defined by equation (7) is used to represent the changes of temperature [12, 18] \(T\) is mimicked by the amplitude \(A\), and the cooling rate is defined by \(dA/dt\). In subsequent simulation, the different thermal conditions were achieved by varying the amplitude \(A\), and the total computing time steps.

4.1. Liquid-glass-crystalline phase transition
As the super-cooled liquid cools from a high temperature to a low one, there are two possible phase changes: liquid to crystalline or liquid to glass, mainly depending on the compositions and cooling rates.

In a particle system, the radial distribution function (RDF) [20, 21], \(G(r)\) is normally used to describe the probability of the location of particles relative to the reference point, and to quantify the
number density or co-ordination number of a particular group of particles relative to the reference point. RDF is widely used to describe the characteristics of disordered molecular systems, such as liquids and amorphous alloys. To quantify the structure of the disordered amorphous alloys, we used the partial radial distribution function (PRDF) to describe how atoms are radially packed relative to the reference atom of the same species.

**Figure 1.** A series of $G(r)$ of atom A at different temperatures, which is offset vertically by $1*n$ different cooling rates, which is offset vertically with $n = 0, 1, ..., 4$. The inset shows the zoom-in first peak of all curves without offset.

**Figure 3.** A series of $G(r)$ of atom A at different cooling rates, which is offset vertically by $1*n$ with $n = 0, 1, ..., 6$. The inset shows the zoom-in first peak of all curves without offset.

Figure 1 shows the partial radial distribution function of atom A at different isothermal temperatures. By comparing the characteristics of the first peaks, mainly the sharpness of the peaks, and the full-width-at-half-maximum (FWHM). It clearly shows that from $A = 0.01$ to $A = 0.00001$, the first peaks become shaper and shaper, and their corresponding FWHM become smaller and smaller, especially at $A = 0.00001$, the second minor peak start to emerge, showing a typical crystalline feature. In order to quantify the ordered, and disordered atomic structures, we define that the structure with $H < 2.0$ and FWHM > 1.2 as pure random liquid structure, that with $2.5 < H < 3.0$ and $0.5 < $FWHM$ < 1.2$ as glassy (short plus medium range ordered) structure and that with $H > 3.0$ and FWHM < 0.5 as crystalline structure.

4.1.1. Order to disorder transition at different cooling rates. Based on the above analysis and definition, in the simulation, we “quench” the liquid with purely random atomic structure simulated at $A=0.01$ (high temperature) to $A=0.00001$ (low temperature) with a series of different cooling rates, i.e. $dA/dt =1.00E-06$ to $dA/dt = 5.00E-08$.

Figure 2 shows the simulated patterns for the atomic configuration at different cooling rates, and the corresponding $G(r)$ curves for each pattern are shown in figure 3. Clearly, the maximum of first peaks of $G(r)$ changes from 2.31 to 3.32 and the FWHM from 0.78 to 0.45 with the decrease of the cooling rates, and the corresponding patterns become more and more orderly arranged. Compared to the pattern shown in figure 2a, those in figure 2b, c have more medium range ordered clusters with the decrease of the cooling rates. Further decrease in cooling rates give enough time for the random atoms in liquid to grow into crystal-like clusters as showed in figure 2d, e, f. It is interesting to note that a small peak on the immediate right side of the first peaks start to emerge with the decrease of cooling rates, especially at $dA/dt=1.33E-07$ to $dA/dt=5.0E-08$. 

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Figure 2. The simulated atomic configurations for the binary alloy using different cooling rates: (a) \( \frac{dA}{dt} = 4.0 \times 10^{-7} \), (b) \( \frac{dA}{dt} = 2.0 \times 10^{-7} \), (c) \( \frac{dA}{dt} = 1.33 \times 10^{-7} \), (d) \( \frac{dA}{dt} = 1.0 \times 10^{-7} \), (e) \( \frac{dA}{dt} = 6.66 \times 10^{-8} \), (f) \( \frac{dA}{dt} = 5.0 \times 10^{-8} \).

4.2. Order-to-disordered transition across the amorphous-crystalline interface

In order to study the atomistic order to disordered transition across the interface between the crystalline and amorphous phase, the simulation domain is purposely enlarged as \( N_x = 512, N_y = 256 \), and treated as two equal sized domain (each has \( N_x = 256, N_y = 256 \)), in which different cooling rates (see section 4.2.1), and also chemical compositions represented by the ratio of number density (see section 4.2.2), were used to produce a diffuse interface at the interface between the two domains.

4.2.1. The effects of cooling rates. In the simulation, the left half-domain is calculated using low cooling rate, \( \frac{dA}{dt} = 5.0 \times 10^{-8} \), and the right one with high cooling rate \( \frac{dA}{dt} = 2.0 \times 10^{-7} \). The whole domain is quenched from super-cooled liquid with a high temperature \( A = 0.01 \).

Figure 4a-d show the supercooled liquid state at \( A = 0.01 \), from which two different cooling rates are applied on left and right part of computation domain respectively to create a diffuse interface. The left part is quenched with a slow cooling rate, and therefore the atoms have enough time to diffuse and grow into crystalline-like clusters. While the right part experiences a slowing down of the atom movement because of fast cooling rate applied (right half of figure 4b). As time evolves, the left part completely freezes into crystalline solid (figure 4d), while the right parts starts to nucleate and form median range ordered crystals.

Figure 4b and c show a clear interface because of the different cooling rate generated different atomic configuration, and the interface separates the two domains that contain different size and orientation of crystals. Although the simulated medium range-ordered structure can relax quickly into crystalline-like structure, this model shows that this transition can be captured elegantly during the simulation.
4.2.2 The effect of number density (composition). As discussed in [12], the composition in at % increases linearly with the increment of number density if \( n_i \leq 1.5 \). Therefore, variations of number density can be used to represent the chemical composition changes in real material systems.

The effect of different compositions on the order-to-disordered atomistic structure transition is studied by varying the ratio of number density, \( n_A \) and \( n_B \). Similar to section 4.2.1, the computational domain consists of left and right halves. \( n_A = 0.1 \) (denoted by red particles in figure 5), \( n_B = 0.2 \) (denoted by green particles in figure 5) is given to the left part, and \( n_A = 0.2, n_B = 0.1 \) for the right part. The whole domain is again “quenched” from \( A = 0.01 \) to \( A = 0.00001 \) in \( t = 2.0 \times 10^7 \times dt \) time steps to allow enough time for the diffusion of atoms to occur. Figure 5 shows that there is a significant difference in atomistic structure in the two halves at different time. For example, starting from \( t = 1.0 \times 10^7 \times dt \), small clusters of crystals nucleate and appear in the super-cooled liquid in the left half, and grow into medium range ordered crystals as showed in figure 5d. However, the right half remains in a randomly distributed amorphous state throughout. Clearly, the effect of chemical compositions on the transition of amorphous to crystalline structure is again captured elegantly by the PFC model.

5. Conclusion

Phase field crystal model was used to simulate the evolution of atomistic structure of a binary alloy. The atomic structure changes due to the variation of chemical composition and different cooling rates of the alloy system are elegantly simulated by the phase field crystal model. Further validation of the modelled atomistic structures and pair distribution functions against the diffraction data obtained from real metallic glass and composite alloys are under way to establish the link between the dimensionless model parameters employed in simulation and the real alloy composition and thermal conditions during solidification.
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