Defect strength and strain glass state in ferroelastic systems

Dong Wang^{1,2}, Duchao Lv^{1,2}, Yipeng Gao², Yu Wang^{1}, Xiaobing Ren^{1,3} and Yunzhi Wang^{1,2}*

1. Frontier Institute of Science and Technology, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter and State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China
2. Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210, USA
3. Ferroic Physics Group, National Institute for Materials Science, Tsukuba, 305-0047, Ibaraki, Japan

Abstract

It has been shown both experimentally and by computer simulations that stress-carrying defects can change a normal sharp first-order martensitic transformation (MT) to a continuous strain glass transition in ferroelastic systems and offer unique properties. However, strain glass state has been found only in limited ferroelastic systems with relatively small transformation strains such as the trigonal phase (1%) in NiTi-based alloys and the orthorhombic phase (2%) in TiNb-based alloys by means of impurity doping. We show in this paper that there exists a critical value of defect strength relative to the strength of MTs for creating a strain glass state. Using a typical strain glass system, $\text{Ti}_{48.5}\text{Ni}_{51.5}$ with symmetrical anti-site defects, as an example, we show that the equivalent Von Mises strain caused by anti-site defect with randomly distribution (with 3% concentration) is 7/8.9 times of that created by the stress free transformation strain of Martensitic phase in order to produce an R/B19 strain glass state respectively. The maximum interaction energy between the anti-site defects and the martensitic variant is estimated to be 16 times larger than that between different martensitic variants at this defect concentration. This finding may shed light on developing new strain glasses of much larger transformation strains for broader applications through defect engineering.

Keywords: Martensitic transformation, defect engineering, strain glass, phase field method

* Corresponding author:

yuwang@mail.xjtu.edu.cn

1. Introduction

Martensitic transformation (MT) is a diffusionless and shear-dominant solid-state structural phase transformation found in many material systems such as metals, ceramics and even proteins[1-5]. Because of crystal symmetry breaking during the transformation, multiple degenerate, crystallographically equivalent martensitic variants form self-accommodating, long-range ordered domain patterns[2] that underpin the “smart” properties of a ferroelastic system such as shape memory effect (SME) and superelasticity (SE). Crystalline defects (such as point defects, dislocations, precipitates and grain boundaries) have been utilized to alter the transformation pathways and domain structures[6, 7] in ferroelastic systems to tailor their properties[8-10], such as the temperature range of SE and size of hysteresis. Recently, a non-conventional transformation pathway (i.e., strain glass transition) that leads to nanoscale strain domain patterns was reported in TiNi [7, 11-13], Ti-Pd-Cr[14], Au-Cu-Al[15] and TiNb[16] alloys through defect engineering (e.g., by introducing anti-site and interstitial point defects and nano-precipitates). Different from the well studied “precursor” phenomenon (i.e., tweed) [17-20], which is described as a metastable state above the MT start temperature, M_s , this strain glass state can be regarded as a “frozen” precursory state [21] and the system does not transform into normal polytwinned martensite with long-range strain ordering (i.e., a strain crystal) under further cooling. The strain glass (STG) systems are found to have unique properties that are absent in normal martensitic systems, including continuous transformation characteristics, frequency dispersion of storage modulus,

slim hysteresis and low modulus [7, 10, 13, 15, 16, 21-28]. The discovery of this unique strain glass transition (STGT) pathway not only opens a new avenue for theoretical study of different strain states and their distinct properties in ferroelastic systems, but may also lead to the development of new alloys for novel applications in different fields [14, 26, 29].

Since the discovery of the STGT, different models have been proposed [25, 30-34] to explain the physical origin of the STG state. It was shown that local lattice distortion created by point defects plays an important role in changing the transformation pathway from a sharp first-order MT to a continuous STGT and producing nanosized martensitic domains without long-range strain ordering in doped ferroelastic systems. However, experimental observations have shown that not all such defects can change a normal MT to a STGT [5]. Up to now, the STGT has been observed in ferroelastic systems with only limited martensitic structures through doping specific defects. In TiNi-based ferroelastic systems, for example, only specific elements doping (such as excess Ni, Fe, Cr, Mn, but not Cu and Pt) can produce the STG states [12, 13, 28] and the reported STG states are all R(trigonal)-phase STGs (i.e., R-phase nanodomains) [11-13, 28]. There is no report of B19 or B19' STG yet in doped TiNi-based ferroelastic systems, even though B19 or B19' is the most stable martensitic phase found in these alloy systems. Comparing with the small stress-free transformation strain (SFTS) values of the R phase (<1%), a potential B19 or B19' STG may show much wider applications because of their giant SFTS (>8%).

Although there is no doubt that random fields from stress-carrying defects are necessary to create the STG state, a critical “strength” of the stress-carrying defects should exist in a ferroelastic crystal that determines whether its strain state is a strain crystal or a strain glass upon cooling. Such a critical strength may be measured by the relative “strength” of the random strain (lattice distortion) field created by the defects to the transformation strain that has to be accommodated during MTs. Previous studies [25, 31, 33, 34] have focused mainly on the effect of defect concentration on the formation of STG. In this study, we investigate the effect of defect strength at a fixed defect concentration on the transition behavior of a doped ferroelastic system. This may explain the experimentally observed phenomenon that when martensitic systems are doped with the same amount but different types of point defects, some of them become STG systems and some of them remain as martensitic systems. In particular, we identify such critical defect strength using three-dimensional (3D) phase field simulations [23, 30, 35, 36] based on Landau theory of phase transformations [3, 37], gradient thermodynamics [38] and microelasticity theory of two-phase coherent solids [39] in an attempt to address the following key questions concerning STGs: why there is no B19 or B19’ STG states in TiNi-based alloys by impurity doping and what kind of defects can change the normal B19 or B19’ strain crystal (normal martensite) to the corresponding STG.

To measure the relative defect strength, we introduce a defect strength coefficient, ϕ , which is the ratio between the equivalent Von Mises strain of the eigenstrain of a given type of defects and the equivalent Von Mises strain of the stress-free

transformation strain (SFTS) tensor of a given type of MT. A new phase diagram connecting temperature with defect strength coefficient ϕ is established, which describes how the ϕ value alters strain state in NiTi systems. Such a phase diagram may guide defect engineering to develop new STGs of larger transformation strains for broader applications. The simulation results also show that for a symmetrical anti-site defect, the critical defect strength coefficient, $\phi_c=8.9$ is necessary to produce a B19 strain glass.

2. Model

The model systems considered are generic single crystals undergoing improper cubic $\rightarrow$ trigonal (R) and cubic $\rightarrow$ orthorhombic (B19) martensitic transformations, which have relatively small and large transformation strains respectively in NiTi-based shape memory alloys (SMAs).

The Local chemical free energy of the systems is approximated by a sixth-order Landau polynomial typical for improper MTs[35, 40]. The simplest form of such a polynomial reads,

$$f_{ch}(\eta_1, \dots, \eta_n) = \frac{1}{2} A_1 \sum_{i=1, \dots, n} \eta(\mathbf{r})_i^2 - \frac{1}{4} A_2 \sum_{i=1, \dots, n} \eta(\mathbf{r})_i^4 + \frac{1}{6} A_3 \left(\sum_{i=1, \dots, n} \eta(\mathbf{r})_i^2 \right)^3, \quad (1)$$

where η_i ($i=1-n$) are structural order (SO) parameters that characterize the symmetry-related n -fold degenerate transformation pathways (or correspondence variants of martensite). n is determined by the symmetry of both the austenitic and martensitic phases. For a parent phase with a cubic symmetry, the n values for

different martensitic phases including R, O/B19 and B19' are 4, 6 and 12 respectively[2, 41]. The SFTS tensor, $\varepsilon_{ij}^M(p)$ ($p=1-n$), for each of the n -fold degenerate correspondence variants of martensite can be formulated according to the lattice parameters of austenite and martensitic phases and the lattice correspondence between them[2, 41]. The total strain at point $\mathbf{r}$ is given by $\varepsilon_{ij}(\mathbf{r}) = \sum_{p=1}^n \varepsilon_{ij}^M(p) \eta(\mathbf{r})_p^2$, where, $\varepsilon_{ij}^M(p)$ is the tensor of the transformation strain and n is the number of martensitic variants. Thus the crystal structure at the point $\mathbf{r}$ is represented by the value of the order parameters, e.g., $(\eta_1, \eta_2, \dots, \eta_n) = (0, 0, \dots, 0)$ represents the austenite (cubic) and $(\eta_1, \eta_2, \dots, \eta_n) = (\eta_0, 0, \dots, 0), (0, \eta_0, \dots, 0), \dots$, or $(0, 0, \dots, \eta_0)$ represents one of the martensitic variants, where η_0 is the equilibrium value of the structural order parameter.

In Eq. (1) $A_1 = A_1^0 \cdot (T - T^0(c))$, A_1^0, A_2, A_3 and A_4 are positive constants, c is average defect concentration in the simulations, $T^0(c) = T^{00} + b \cdot c$ ($T^{00} = 300, b = -300$, and $c = 0.03$), and b characterizes the relative strength of the global transition temperature effect (GTTE) associated with point defects[25]. The GTTE describes how the doped anti-site defects alter the average thermodynamic stability of martensite and change the transition temperature of the whole system. We assume that it does not create spatial variation of the Landau potential.

In contrast, the local stress field effect (LFE) associated with local lattice distortions [25, 42], $\varepsilon_{ij}^{local}(\mathbf{r})$, caused by the point defects creates spatial variation and symmetry-breaking of the Landau potential[25]. The excess energy associated with

the LFE can be described by the following equation[23, 25]

$$f_L(r) = C_{ijkl} \sum_{i,j,k,l=1,2,3} \varepsilon_{ij}^{local}(\mathbf{r}) \cdot \varepsilon_{kl}^M(\mathbf{r}), \quad (2)$$

where $\varepsilon_{kl}^M(\mathbf{r})$ describes the SFTS of the martensite phase.

Note that both strains and shuffles are two important modes of the MTs considered in this study. Since the focus of the current work is on the effect of interplay between the transformation strain and the eigenstrain of defects, and the transformation strain is independent of shuffle, the shuffle modes are ignored in this paper.

The non-local gradient energy, $f_{gr}(\eta_1, \dots, \eta_n)$, associated with spatial non-uniformity of the SO parameters[38], can be approximated by

$$f_{gr}(\eta_1, \dots, \eta_n) = \frac{1}{2} \beta \left(\sum_{i=1, \dots, n} (\nabla \eta_i)^2 \right) \quad (3)$$

where β is the gradient energy coefficient;

The coherency elastic strain energy, E_{el} , associated with the lattice mismatch between the austenite and martensite and among different variants of the martensitic phase, formulated based on Khachaturyan's microelasticity theory[30, 39], is given by

$$E_{el} = \frac{1}{2} C_{ijkl} \sum_{p=1}^n \sum_{q=1}^n \varepsilon_{ij}^M(p) \varepsilon_{kl}^M(q) \int \eta_p^2(\mathbf{r}) \eta_q^2(\mathbf{r}) d^3r - \frac{1}{2} \sum_{p=1}^n \sum_{q=1}^n \int \frac{d^3k}{(2\pi)^3} B_{pq}\left(\frac{\mathbf{k}}{k}\right) \{\eta_p^2(\mathbf{r})\}_k \{\eta_q^2(\mathbf{r})\}_k^*, \quad (4)$$

where C_{ijkl} is the elastic modulus tensor, $\mathbf{k}$ is the wave vector defined in the reciprocal space, $\{\eta_p^2(\mathbf{r})\}_k$ is the Fourier transform of $\eta_p^2(\mathbf{r})$, $\{\eta_p^2(\mathbf{r})\}_k^*$ is the conjugate of

$\{\eta_p^2(\mathbf{r})\}_k$, and the kernel $B_{pq}(\mathbf{k}/k)$ is $B_{pq}(\mathbf{e}) = e_i \sigma_{ij}^0(p) \Omega(\mathbf{e})_{jk} \sigma_{kl}^0(q) e_l$, where $\mathbf{e} = \mathbf{k}/k$, $\sigma_{ij}^0(p) = C_{ijkl} \varepsilon_{ij}^M(p)$, $\Omega(\mathbf{e})_{ij}^{-1} = C_{ijkl} e_k e_l$. The SFTS of the martensitic phase can be described in terms of the order parameter fields, i.e., $\varepsilon_{ij} = \sum_{p=1}^n \varepsilon_{ij}^M(p) \eta_p^2$.

The total free energy of the system, F , consists of all the above contributions, i.e.,

$$F = \int d^3\mathbf{r} [f_{ch}(\eta_1, \dots, \eta_n) + f_L + f_{gr}(\eta_1, \dots, \eta_n)] + E_{el}, \quad (5)$$

and its variational derivatives with respect to the order parameter fields form the thermodynamic driving force for microstructure evolution during transitions among different strain states (i.e., austenite, martensite and strain glass) characterized by the order parameters, following the stochastic time-dependent Ginsburg-Landau equation:

$$\frac{d\eta_p(\mathbf{r}, t)}{dt} = -M \frac{\delta F}{\delta \eta_p(\mathbf{r}, t)} + \xi_p(\mathbf{r}, t), \quad p = 1, \dots, n \quad (6)$$

where ξ is the Langevin noise term describing thermal fluctuations and M is the dynamic coefficient.

To compare two different strain tensors (defect distortion and SFTS of martensite), we define a defect strength coefficient ϕ , which can be calculated as the ratio of the equivalent Von Mises strain caused by defect and the equivalent Von Mises strain caused by the martensitic phase transformation, i.e., $\phi = \frac{|\varepsilon_{eq}^{defect}|}{|\varepsilon_{eq}^{SFTS}|}$, where the

equivalent Von Mises strain can be calculated as

$$\varepsilon_{eq} = \frac{2}{3} \sqrt{\frac{3(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2)}{2} + \frac{3(\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{13}^2)}{4}}. \text{ For example, consider an anti-side defect}$$

in NiTi, where an additional Ni atom occupies the Ti-sublattice in a B2 unit cell and

changes it to a BCC unit cell of Ni (Fig. 1). This will create a dilational strain with a

$$\text{maximum value: } \varepsilon^{defect} = \begin{pmatrix} -0.075 & 0 & 0 \\ 0 & -0.075 & 0 \\ 0 & 0 & -0.075 \end{pmatrix} \quad (\text{i.e., } \frac{a_{bcc}^{Ni} - a_{B2}^{NiTi}}{a_{B2}^{NiTi}}) \text{ with Von Mises}$$

strain $\varepsilon_{eq}^{defect} = 0.1061$. According to the SFTS of the R phase [23, 43], i.e.,

$$\varepsilon^R = \begin{pmatrix} -0.000246 & 0.006038 & 0.006038 \\ 0.006038 & -0.000246 & 0.006038 \\ 0.006038 & 0.006038 & -0.000246 \end{pmatrix}, \text{ the equivalent Von Mises strain is}$$

$$\varepsilon_{eq}^R = 0.01207, \text{ and we have the coefficient } \phi_R^{Ni} = \frac{\varepsilon_{eq}^{defect}}{\varepsilon_{eq}^R} = 8.76 \text{ for Ni doping. In the}$$

present work, we change the value of lattice distortion of ε^{defect} and alter the coefficient ϕ to determine the critical value of defect strength in the formation of strain glass. The dimensionless materials parameters [23] used in our simulations are listed in Table. 1. The system size considered is $64\text{nm} \times 64\text{nm} \times 64\text{nm}$ with a $64 \times 64 \times 64$ numerical mesh and periodical boundary conditions are applied along all three dimensions. Need to note, we assume that the phase field voxels which contain defects produce a distortion strain ε^{defect} in our simulations, and the dimensionless concentration c describe the volume fraction of phase field voxels including defects. The dimensionless defect concentration is fixed to $c=0.03$ in our simulations.

3. Results

3.1. Critical defect strength for the formation of R strain glasses

Fig. 2 shows the calculated volume fraction of R martensite transition upon

cooling and heating with different defect strength coefficient ϕ . When $\phi=0.0$ (defect free), Fig.2 (a) shows typical first order transition characteristics (i.e., sharp change of the volume fraction at the transition temperature) upon cooling and large temperature hysteresis under thermal cycling. When the defect strength $\phi < 7.0$ (Figs. 2 (b) -(d)), the volume fraction change is still sharp and the temperature hysteresis under thermal cycling is still obvious but become smaller and smaller. When $\phi \geq 7.0$, the systems show gradual change of the volume fraction with almost zero temperature hysteresis as shown in Figs. 2 (e-f). These results show that increasing defect strength at fixed defect concentration can suppress normal MT and change it to a continuous transition.

Fig. 2(g) summarizes the variation of temperature hysteresis as function of defect strength coefficient ϕ , showing a continued decrease of the hysteresis as ϕ increases and, when $\phi \geq 7.0$, the hysteresis vanishes. The vanishing of hysteresis in temperature cycle implies a continuous transition, and this special defect strength coefficient can be defined as the critical value of R strain glass transition (i.e., $\phi_c=7.0$) in the model system. Note that the critical defect strength coefficient ϕ_c varies with defect concentration, as shown in Fig. 3. The lower is the defect concentration, the higher is the defect strength needed to produce a strain glass state. This result is consistent with the experimental observations that different dopants (such as Ni and Fe anti-site defects) require different critical defect concentrations for the R strain glass transition, e.g., $\text{Ti}_{48.5}\text{Ni}_{1.5}$ [28] and $\text{Ti}_{50}\text{Ni}_{44}\text{Fe}_6$ [13]. In excess Ni doped NiTi system, the defect strength coefficient $\phi_R^{\text{Ni}} = 8.76$, which is larger than the critical value $\phi_c=7.0$, so the system can become an R strain glass with excess Ni doping.

Based on the temperature dependence of volume fraction of martensite shown in Figs. 2(a)-(f), we establish a temperature vs. defect strength phase diagram (Fig. 4) with fixed defect concentration $c=0.03$. In this phase diagram, T_S describes the start temperature of martensitic phase transformation or strain glass transition, and T_F describes the finish temperature of these transitions. T_S is defined as the temperature at which the volume fraction of martensite reaches 5% and T_F is defined as the temperature at which the volume fraction of martensite reaches 90%. The phase diagram indicates that the gap between T_S and T_F increases when the defect strength increases. In addition, T_S shows almost a linear increase with defect strength, which indicates that the defect strength defined in the current study represents reasonably well the potency of the anti-site defects for inducing martensitic domains. In contrast, T_F shows a non-monotonic dependence on the defect strength. Although the anti-site defects promote nucleation of martensite, they suppress autocatalysis and confine the growth when their strength becomes high enough because of their randomness in space.

The insets in Fig. 4 describe the corresponding microstructural states at different defect strength and temperature, where red, blue, yellow and green represent the four variants of the R martensitic phase, and the austenite is transparent. Clearly as the defect strength increases the self-accommodating, long-range ordered twinning martensite changes gradually into randomly distributed nano-domains of individual martensitic variants. In between T_S and T_F , there exist precursory nanodomains (twined) and, below T_F , the system transforms either to well-defined, internally

twinned martensite when the defect strength $\phi < 3.5$ or to a strain glass (identified by the vanished temperature hysteresis shown in Fig. 2) when defect strength $\phi \geq 7.0$ (i.e., ϕ_c). Note that the transition from a strain crystal to a strain glass when defect strength increase is rather diffuse.

3.2. Critical defect strength for B19 strain glass

The above simulation results show that the critical defect strength for the formation of R strain glass is $\phi_c = 7.0$, which is less than the maximum value of $\phi_R^{Ni} = 8.76$ when excess Ni replaces Ti and forms anti-site defects in NiTi. This explains why experimental observations have shown R strain glasses in NiTi-based ferroelastic systems. In order to understand why there is no B19/B19' strain glass discovered in TiNi-based alloys, we calculate the critical defect strength for B19 strain glass transition in the same system (defect concentration is also fixed to 0.03). Note that we choose B19 not B19' because B19 have less number of martensitic variants which may save the simulation time. The typical SFTS of B19 is used

$$\varepsilon^{B19} = \begin{pmatrix} 0.02915 & 0 & -0.02915 \\ 0 & -0.0421 & 0 \\ -0.02915 & 0 & 0.02915 \end{pmatrix} [2] \text{ and its eigenvalues are } -0.0421, 0, \text{ and}$$

0.0583. Thus we have $\varepsilon_{eq}^{B19} = 0.0587$ and we have defect strength coefficient

$$\phi_{B19}^{Ni} = \frac{\varepsilon_{eq}^{defect}}{\varepsilon_{eq}^{B19}} = 1.27 \text{ (Ni replace Ti) and } \phi_{B19}^{Cu} = \frac{\varepsilon_{eq}^{defect}}{\varepsilon_{eq}^{B19}} = 0.71 \text{ (Cu replace Ni). The}$$

calculated volume fraction change upon cooling and heating for different defect strength coefficients ϕ are shown in Fig. 5. The results show that the temperature hysteresis changes to a constant (close to zero) when the defect strength $\phi \geq 8.9$ (Fig. 5

(g)). Thus the critical defect strength coefficient for the formation of a B19 strain glass is $\phi_c \sim 8.9$. Fig. 5(h) shows the corresponding microstructures of B19 martensite obtained at different defect strength.

The above simulation results show that both B2 $\rightarrow$ R and B2 $\rightarrow$ B19 martensitic transformations can be suppressed into strain glass transitions when the defect strength ϕ is larger than a critical value, e.g., $\phi_c = 7.0$ for R strain glass and $\phi_c = 8.9$ for B19 strain glass. However, the B19 martensite has much larger energy values of the SFTS and thus the Von Mises strain. The formation of B19 strain glass would require a much larger value of the dilational strain from an anti-site defect, e.g., $\varepsilon_{eq}^{defect} \cong 0.52$ according to the definition of the defect strength coefficient ϕ (introduced earlier), which is impossible for point defects doping. This may explain why there is no B19 strain glass found in TiNi-based systems.

As mentioned earlier, it is the interplay between self-accommodation among different martensitic variants and random fields associated with stress-carrying defects that determines the transformation paths leading either to a strain crystal or to a strain glass in a ferroelastic system upon cooling. To characterize such an interplay we plot the relationship between the ratio of defect-martensite interaction energy and martensite-martensite interaction energy, $\frac{E_{M-D}^{max}}{E_{M-M}^{max}}$, obtained from the phase field simulations and defect strength coefficient ϕ in Fig. 6. E_{M-D}^{max} describes the maximum interaction energy between a single anti-site defect and a martensitic variant, and E_{M-M}^{max} describes the maximum interaction energy between different martensitic

variants. ϕ_C^R and ϕ_C^{B19} are the critical defect strength coefficients for R strain glass and B19 strain glass, respectively, according to Fig. 1 and Fig. 5. At the critical defect strength for B19 strain glass, ϕ_C^{B19} , $\frac{E_{M-D}^{\max}}{E_{M-M}^{\max}} = 16$. This indicates that the defect–martensite interaction energy must be sixteen times of the martensite–martensite interaction energy in order to produce a B19 strain glass state (at this concentration 0.03). Note that this critical value of the defect-martensite interaction energy will be different when the defect concentration changes. A higher defect concentration in general will require lower defect-martensite interaction energy.

4. Discussions

The above simulation results suggest the existence of a critical defect strength ϕ to induce a strain glass transition in doped ferroelastic systems and explain why B19 strain glass is difficult to form in the NiTi system. In this part, we try to explore the physical origin through calculating the extra interaction caused by defect (by using R strain glass as example). Fig. 7 shows the local stress field caused by a single anti-site defect in the centre of a simulation cell of 64nm cube under periodical boundary condition in all three dimensions. The local stress field was calculated using Khachaturyan's microelasticity theory[39] by using the eigenstrain of the anti-site defect (as illustrated in Fig. 1). Figs. 7(a)-(f) show the stress field distribution of σ_{11} , σ_{22} , σ_{33} , σ_{12} , σ_{13} and σ_{23} , respectively, around the anti-site defect, where the purple and light blue colors describe the isosurfaces of the tensile and compress stress fields,

respectively. The existence of stress field will produce different interactions between the defect and different martensitic variants and will influence the microstructural state. Fig. 7(g) shows the negative excess interaction energy calculated for different martensitic variants in the local stress field of the anti-site defect. It shows that this anti-site defect prefers certain martensitic variants (negative values) and suppresses some others (positive values) at different locations. Because the anti-site defects are randomly distributed in space, the interaction energy fields are random as well, causing the thermodynamic frustration.

The change of defect strength affects directly the amplitudes of the local stress fields and, hence, the degree of the frustration. Fig. 8(a) and (b) show the stress amplitude distributions (potency distribution) of local stress fields σ_{11} and σ_{12} created by the anti-site defects in $\text{Ti}_{48.5}\text{Ni}_{51.5}$ obtained from the phase field simulations with different defect strength coefficient ϕ . Such a distribution is calculated through counting the numbers of volume elements that have the same local stress value within a given defect strength coefficient in the entire system. Because our simulations use symmetrical anti-site defects and their eigenstrains are purely dilatational, the other stress components (σ_{22} , σ_{23} , σ_{33} , σ_{13} ,) should have similar amplitude distributions as either that of σ_{11} or that of σ_{12} . The calculation results show that the stress amplitude distribution becomes broader when the defect strength coefficient ϕ increases. The broader stress amplitude distribution will produce more influence area with high interaction as shown in Fig. 8(c) and prevent the formation of ordered ground state (twinned M). Instead, the system forms a glassy state (i.e., randomly distributed

nanodomains of individual variants of martensite). The broad distribution of activation energy due to contributions from interaction energy caused by defects (i.e., potency distribution of the defects) as shown in Fig. 8 (c) is the key effect of the continuous strain glass transition process in doped ferroelastic systems. This broad distribution of activation energy will lead to a broad martensite nucleation temperature and smooth transition. Fig. 9 (a) shows the spatial distribution of phase field voxels containing defects in the system, Figs. 9(b)-(f) show the spatial distribution of Local Von Mises stress (σ_{VM}) caused by defects with different defect strength coefficient ϕ , where, Local Von Mises stress can be calculated: $\sigma_{VM} = \sqrt{\frac{(\sigma_{11}-\sigma_{22})^2+(\sigma_{11}-\sigma_{33})^2+(\sigma_{22}-\sigma_{33})^2+6(\sigma_{12}^2+\sigma_{23}^2+\sigma_{13}^2)}{2}}$. With the increase of defect strength coefficient ϕ , the local stress distribution caused by defects becomes more inhomogeneous. Simultaneously, the volume of high stress regions (green and yellow color) increase and these regions are separated by low stress regions (blue color) when defect strength coefficient is high (see Fig. 9(e) and (f)). High stress regions prefer the nucleation of M domains but the local stress regions limits the growth. The randomly distributed local stress field influences the nucleation and growth of martensitic domains and should be the physical origin of strain glass transition.

The change of the total free energy of the systems (R martensite and R strain glass) upon cooling calculated for different defect strengths are shown in Fig. 10. $\phi=0.0$ and $\phi=3.5$ describing the free energy changes accompanying normal martensitic transformations (with the formation of long range ordered, internally twinned martensitic plates) and $\phi=7.0$ and $\phi=8.76$ describing the free energy

changes accompanying the strain glass transitions (with the formation of nanosized martensitic domains). Fig 10 (a) shows the changes of the local chemical free energy, F_{ch} , calculated according to Eq.(1). All the chemical free energy curves with different defect strengths show a decrease upon cooling. The chemical free energy curves of $\phi=0.0$ and $\phi=3.5$ show a sudden change at transition temperature, while the chemical free energy curves of $\phi=7.0$ and $\phi=8.76$ show a gradual change upon cooling. Furthermore, the chemical free energy curves show almost the same driving force (i.e., the free energy difference between the highest and lowest temperatures) upon cooling for both normal martensite ($\phi=0.0$ and $\phi=3.5$) and strain glass ($\phi=7.0$ and $\phi=8.76$). The chemical free energy of strain glass is a little higher than that of the internally twinned martensite because there exist more domain boundaries in the strain glass system. Figs. 10 (b) and (d) show the non-local gradient energy, F_{gr} (Eq. (3)), and the coherency elastic strain energy, F_{el} (Eq. (4)), respectively. Both gradient energy and elastic strain energy show an increase upon cooling with different defect strength coefficients. The gradient energy and elastic strain energy curves obtained for $\phi=0.0$ and $\phi=3.5$ show small increases with the formation of long range ordered, internally twinned martensite upon cooling, while the gradient energy and elastic strain energy curves for $\phi=7.0$ and $\phi=8.76$ show huge increases with the existence of randomly distributed nanosized martensitic domains. The long range ordered, internally twinned martensitic states (in $\phi=0.0$ and $\phi=3.5$) include a low density of domain boundaries with atypical twin structure, which results in the minimum elastic strain energy and gradient energy. On the contrary, the glassy martensitic states (in $\phi=7.0$ and $\phi=8.76$)

include irregular shaped martensitic nanodomains with a large density of domain boundaries, which increase both the elastic strain energy and gradient energy. In the view of elastic energy and gradient energy, strain glass state (with high ϕ) should be unstable because it includes much higher energy than that of twin martensite (with low ϕ). However, the fact is different (i.e., strain glass state with nanosized martensitic domains is stable when $\phi=7.0$ and $\phi=8.76$), defects must produce extra interaction in stabilizing this disorder state. Fig. 10 (c) shows the excess free energy F_L (i.e., the extra interaction energy) caused by point defects according to Eq. (2). The excess free energy shows a decrease upon cooling when ϕ is not equal to zero. The excess free energy of $\phi=3.5$ shows a small decrease with sudden change, while the excess free energy of $\phi=7.0$ and $\phi=8.76$ show a large decrease with gradual change. The excess energy caused by point defects provides an extra driving force to compensate the high elastic energy and gradient energy and stabilize the system to a glassy martensitic state. Fig. 10 (e) shows the total free energy F_{total} (Eq. 5) of the whole system with different defect strength. The total free energy shows a decrease for both martensitic transition (in $\phi=0.0$ and $\phi=3.5$) and strain glass transition (in $\phi=7.0$ and $\phi=8.76$) upon cooling. It describes that both the formation of nanodomains at $\phi=7.0$ and $\phi=8.76$ and the formation of twin martensite at $\phi=0.0$ and $\phi=3.5$ upon cooling are reasonable. It implies that strength of doped defects is the most important effect to change the phase transition pathway from first order martensitic transformation to continuous strain glass transition. To separate the effect of defect strength, we calculate the total free energy without the excess free energy F_L as shown

in Fig. 10(f). The free energy curves of $\phi=0.0$ and $\phi=3.5$ in Fig. 10 (f) don't show big difference from that of Fig. 10 (e), which describes that the extra interaction caused defects is too small to suppress normal martensitic transformation when the strength coefficient is small. Differently, the free energy curves of $\phi=7.0$ and $\phi=8.76$ in Fig. 10(f) have shown huge difference from that of Fig. 10 (e), which describes that the extra interaction caused by defects must be large enough to suppress the normal MT when the defect strength coefficient is larger than critical value.

To clarify the frustration effect of F_L caused by point defects, Fig. 11 shows the free energy evolution with initial nanosized martensitic domain state (from $\phi=7.0$) and then evolve with removing the excess energy F_L . The black dot shows the initial total free energy with the nanosized martensitic domain state at $T=0.8T_0$ and $\phi=7.0$. The blue circles describe the free energy change with time after removing the F_L (but keep the initial nanodomain microstructure) in our simulations (i.e., $T=0.8T_0$ and $\phi=0.0$). The free energy curve shows a decrease, which implies that nanosized domain state (strain glass state) will not be stable any more if there is no interaction caused by defects. Insets show related microstructural evolution with time. The microstructures evolutions show that the nanosized martensitic state will grow and change into long range ordered twin martensitic state (i.e., the ground state). Our calculations confirm that the value of interaction effects caused by F_L play a key role in suppressing the long range ordered martensite and stabilizing the nanosized martensitic domains, which depends on the defect strength coefficient.

The competition between the interaction caused by defect and martensitic variants and the interaction caused by different martensitic variants is the physical origin of frustration and the formation of glassy martensitic states in doped ferroelastic systems. Small lattice distortion caused by certain defects may produce too weak interaction to frustrate normal twinned martensitic state with large SFTS. The equivalent Von Mises strain of STFS of B19 phase is about six times larger than that of R phase, which results in a larger driving force for the formation of B19 twin martensitic state[5]. So a larger defect strain caused by point defects is needed to produce large enough extra interaction than that of R phase. Similarly, B19' phase transition has a larger value of eigenvalue of STFS than that of B19, which means that the formation of B19' nanodomains also need much larger value of the lattice distortion strain. Our simulations also imply that the doped anti-site defects (Ni, Fe, Cu...) in TiNi-based alloys will be difficult to produce such a large lattice distortion ($\epsilon_{eq}^{defect} \approx 0.5$) to produce B19/B19' strain glass, other stress-carrying defects (e.g., precipitates, dislocations, grain boundaries) which can produce larger extra interaction must be created to produce this kind of strain glass. Dislocation loops which can produce a Von Mises strain ~ 0.5 will be a possible way to influence normal MT[44] and produce B19/B19' strain glass. In addition, recently experiments show that nano-grains with huge grain boundaries can confine the nucleation and growth of B19' Martensite and produce B19' strain glass[10]. Precursory phase decomposition with compositional and structural non-uniformity can also produce strain glass[22]. More work are needed in future to study relationship between different defect types and different

martensitic phases.

4. Summary

In summary, we study the strain glass transition in doped ferroelastic systems through phase field simulations. The role of lattice distortion caused by stress-carrying defects are studied and a phase diagram including temperature and defect strength is established. A defect strength coefficient which describes the ratio between the equivalent Von Mises strain caused by defect and the equivalent Von Mises strain caused by the martensitic phase transformation is defined in our simulations. We show that the critical defect strength coefficient for the formation of R glassy martensitic state at $c=0.03$ is about $\phi=7.0$. When the defect strength coefficient ϕ is larger than this critical value, the system will be changed from normal first order martensitic transition with large hysteresis into continuous strain glass transition with small hysteresis. The free energy calculations show that the value of excess energy caused by doped point defects play key role in suppressing the long range ordered martensitic twin and stabilizing the glassy martensitic state. Through calculating the critical defect strength's effect for both R phase and B19 phase, our simulations imply that the formation of B19 strain glass also need a larger critical defect strength coefficient i.e., $\phi=8.9$. Considering the larger eigenvalue of SFTS of B19, equivalent Von Mises strain caused by defect must be much larger than that of R strain glass to form B19 strain glass. This explains the puzzle that why there is only strain glass with local R local structure (not B19 or B19') in TiNi-based ferroelastic

systems. Our simulations may shed light on the development of new shape memory alloys with nanosized martensitic domains structure and small hysteresis through defect engineering using extended defects such as dislocations and grain boundaries rather than point defects.

Acknowledgments:

The work was supported by National Basic Research Program of China (2012CB619402, 2014CB644003 and 2010CB631003), National Natural Science Foundation of China (51201125, 51471127, 51071117, 51171140), China Postdoctoral Science Foundation (2012M511996) and 111 Project of China (B06025); the U.S. Natural Science Foundation Grant No. DMR-1410322 (Yunzhi Wang) and US Department of Energy Grant No. DE-SC0001258 (Yipeng Gao); and the Japan KAKENHI (Xiaobing Ren).

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Figure and Table Captions

Figure 1 Schematic figure for the model system (NiTi alloys) with doping, left figure show the defect-free B2 unit cell, right figure shows BCC unit cell caused by excess Ni doped in B2 NiTi system.

Figure 2 (a)-(f) calculated volume fraction of R martensite phase/domains for different defect strength coefficient ϕ in defect concentration $c=0.03$ upon cooling (black) and heating (red). (g) The temperature hysteresis (ΔT) upon cooling and heating with different defect strength ϕ . ϕ_c is the critical defect strength coefficient value resulting in an almost zero hysteresis. The temperature hysteresis is calculated through measuring the temperature difference between cooling and heating when the volume fraction of martensite is 50%.

Figure 3 The critical defect strength coefficient ϕ_c of R strain glass transition for different defect concentration according to temperature hysteresis simulations.

Figure 4 Calculated phase diagram of R martensitic phase transition/strain glass transition upon cooling with different defect strength ϕ in $c=0.03$. T_S describes the phase transition start temperature where the volume fraction of martensite is 5%, T_F describes the phase transition finish temperature where the volume fraction of martensite is 90%. Insets describe the related microstructure, red, blue, yellow and green colors describe the four variants of R martensitic phase respectively.

Figure 5 (a)-(f) calculated volume fraction of B19 martensite phase/domains for

different defect strength coefficient ϕ at $c=0.03$ upon cooling and heating (arrows). (g) The temperature hysteresis (ΔT) upon cooling and heating with different defect strength coefficient ϕ . ϕ_c is the critical coefficient value resulting in an almost zero hysteresis. (h) The microstructure of B19 phase at low temperature with different defect strength coefficient, different colors describe different martensitic variants respectively.

Figure 6 The ratio between calculated maximum interaction energy of single defect-martensitic variants ($E_{M-D}^{\max}$) and maximum interaction energy of different martensitic variants ($E_{M-M}^{\max}$) changes as a function of defect strength coefficient ϕ at $c=0.03$. ϕ_C^R and ϕ_C^{B19} describe the critical defect strength coefficient for R strain glass and B19 strain glass according to Fig. 2 and Fig. 5.

Figure 7 Stress field of (a) σ_{11} , (b) σ_{22} , (c) σ_{33} , (d) σ_{12} , (e) σ_{13} , (f) σ_{23} caused by a single defect ($\phi=8.76$) in the center of the system (black color), purple and light blue colors represent the positive and negative values of the stress value respectively. (g) Negative excess interaction energy (low martensitic phase nucleation barrier) between different R martensitic variants and the defect; red, blue, green and yellow colors represent energy favored 4 R martensitic variants respectively.

Figure 8 Calculated stress field distribution probability of (a) σ_{11} and (b) σ_{12} in $c=0.03$ with different defect strength (from $\phi=1.75$ to $\phi=8.76$). (c) The distribution probability of interaction energy between local stress field caused by point defects and martensitic variant 1 with different defect strength (from $\phi=1.75$ to $\phi=8.76$).

Figure 9(a) Spatial distribution of simulation grids containing point defects (white color). (b)-(f) Spatial distribution of local Von Mises stress (σ_{VM}) caused by point defects with different defect strength coefficient ϕ .

Figure 10The calculation of average free energy density change of the whole system upon cooling with different defect strength(from $\phi=0.0$ to $\phi=8.76$) at $c=0.03$. (a) Local chemical free energy, F_{ch} .(b) The non-local gradient energy, F_{gr} . (c)The excess energy caused by defects, F_L .(d) The coherency elastic strain energy, F_{el} . (e) Total free energy, F_{total} , and (f) Free energy without defects' effect, $F_{total}-F_L$.

Figure 11Average free energy density evolution of the whole system with time after removing defects' effect (i.e., removing excess energy F_L caused by defects) at $c=0.03$. Insets describe the related microstructure evolution. Black dot (black arrow) describes the initial free energy of nanosized martensitic domains got from $T=0.8T_0$ and $\phi=7.0$, blue circles describe the free energy evolution after removing excess energy F_L .

Table 1 The dimensionless parameters (with superscript *) used in our simulations and the relationship between physical and dimensionless parameters.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Table 1

Elastic constants	Energy density	length	Fluctuation	Time	Dimensionless parameters
$C_{ij}^* = C_{ij}/\theta$	$f_{ch}^* = f_{ch}/\theta$ $f_L^* = f_L/\theta$ $f_{gr}^* = f_{gr}/(\theta l_o)$	$\mathbf{r}^* = \mathbf{r}/l_o$	$\xi_p^* = \xi_p/(M\theta)$	$t^* = (tM\theta)/(M^*)$	$C_{11}^* = 2 \times 10^4$, $C_{12}^* = 1.5 \times 10^4$, $C_{44}^* = 5 \times 10^3$, $A_1^{0*} = 20$, $A_2^* = 32.05$, $A_1^{0*} = 37.5$, $\beta^* = 1.5$, $M^* = 1$, $t^* = 1$

An asterisk denotes a dimensionless quantity, $\theta = 10^7 J/m^3$ is the energy scaling factor, $l_o = 1\text{nm}$ is the grid size.