

# Evidence for short-time limit of martensite deaging in shape-memory alloys: Experiment and atomistic simulation

Junkai Deng,<sup>1,2</sup> Xiangdong Ding,<sup>1,3,a)</sup> Zhen Zhang,<sup>1,2</sup> Turab Lookman,<sup>3</sup> Tetsuro Suzuki,<sup>2</sup> Kazuhiro Otsuka,<sup>2</sup> Jun Sun,<sup>1</sup> Avadh Saxena,<sup>3</sup> and Xiaobing Ren<sup>2,b)</sup>

<sup>1</sup>Multidisciplinary Materials Research Center, Frontier Institute of Science and Technology, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

<sup>2</sup>Ferroic physics Group, National Institute for Materials Science, Tsukuba 305-0047, Ibaraki, Japan

<sup>3</sup>Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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It is well known that martensite aging effects in shape memory alloys can be simply removed when the aged martensite experiences a reverse transformation to the parent phase followed by cooling back to the martensite state. This “deaging” process has been known to be very fast but it remains a question as to whether there exists a short-time limit for such a fast deaging process. In this letter, we report that there indeed exists a short-time limit for the deaging. We have studied the aging and deaging of a Au-49.5Cd shape memory alloy, and found that complete removal of the previous aging, as manifested by the recovery of martensite transition start temperature ( $M_s$ ), occurs only after aging in the parent phase for more than 500 s. Shorter time holding/aging in the parent phase results in a higher  $M_s$  as compared with the fully deaged case. Therefore, there is a fast relaxation process during the deaging or parent phase aging process. Atomistic simulations suggest that the origin of the observed time-dependent deaging arises from the change in short-range configurations of point defects, being the same as that of the martensite aging. As a result, it is possible to unify the microscopic mechanism of aging in both martensite and parent phase; both are due to a symmetry-conforming short-range ordering tendency of point defects. © 2010 American Institute of Physics. [doi:10.1063/1.3505494]

For more than half a century, shape memory alloys (SMAs) have been known to exhibit “aging effects” in the martensitic state, i.e., the gradual change in physical properties with time. As aging strongly affects the reliability of SMAs and is undesirable for many applications, many studies have been devoted to understanding the physical origin of aging and how to control it.<sup>1–5</sup> An intriguing aspect of martensite aging is that it can occur even without any detectable change in average structure; this can be explained by a symmetry-conforming short-range ordering (SC-SRO) of point defects,<sup>6,7</sup> which does not alter the average structure or long-range order (LRO).

It has been known that the martensite aging effects can be “annihilated” once the aged martensite undergoes a reverse transformation to the parent phase.<sup>4–6</sup> The martensite formed after this annihilation process recovers the fresh martensite state, as manifested by the recovery of transition temperature. This annihilating process of martensite aging was termed as “deaging.” So far, it has been a common observation that the deaging process seems very fast, as martensite aging seems to disappear completely even after a casual deaging. Therefore, an interesting question arises as to whether there exists a short-time limit for the deaging. If yes, this means that deaging is a time-dependent process, and can be called “parent phase aging.”

In this letter, we found there indeed exists a short-time limit for deaging; martensite aging cannot be removed (as manifested by  $M_s$  temperature) if the deaging time is very short (shorter than 500 s for a Au-49.5Cd SMA). We ob-

served that the deaging or parent phase aging is a fast relaxation process in the parent phase. A combination of molecular dynamics (MD) and Monte Carlo (MC) simulations of the atomic process indicates that the present parent phase aging arises from the change in short-range configuration of point defects, being the same as the martensite aging. Thus it is suggested that there exists a unified microscopic mechanism for both martensite aging and parent phase aging as follows: SC-SRO of point defects.

It is noted that the parent phase aging mentioned here refers to the time-dependent fast deaging process that removes the martensite aging. It is fundamentally different from another “slow parent phase aging,” which is commonly observed in metastable alloys [e.g., Cu–Al–Ni and Au-47.5Cd];<sup>8,9</sup> the latter parent phase aging usually needs several hours (or days) and is related to an early stage of diffusional decomposition or bainite transformation.<sup>8–10</sup> To avoid such an effect, in the present study we used a Au-49.5Cd alloy, which has been known to have martensite as a phase in thermodynamical equilibrium and does not have a decomposition.

We first investigated the time-dependent  $M_s$  during deaging process through the conventional DC four-terminal electrical resistivity measurement. The sample we used was a Au-49.5Cd alloy, which underwent a martensitic transformation (MT) from a cubic parent phase (B2 structure) to a  $\zeta_2'$  martensitic phase (trigonal structure). The sample was first aged in the martensite for 90 days to obtain the well-aged martensite. Then several thermal cycles were carried out sequentially. The sample was heated up to 320 K (parent phase state) each time then followed by cooling down to 295 K (martensite state) with cooling/heating rate 1 K s<sup>−1</sup>. In order

<sup>a)</sup>Electronic mail: dingxd@mail.xjtu.edu.cn.

<sup>b)</sup>Electronic mail: ren.xiaobing@nims.go.jp.

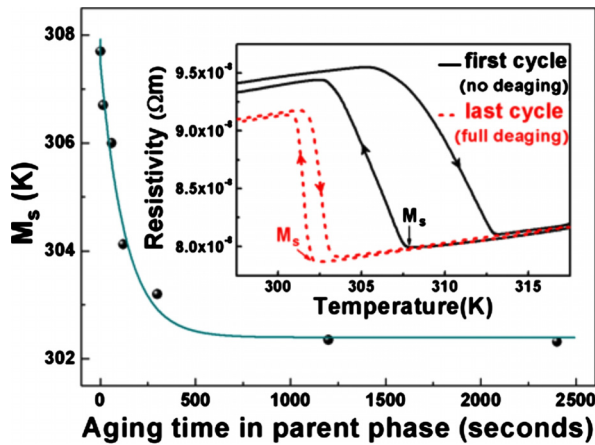


FIG. 1. (Color online) The changes in  $M_s$  temperature of a well-aged martensitic Au-49.5Cd alloy with the aging time in the parent phase, i.e., martensite deaging process. The sample was aged for 0 s, 15 s, 60 s, 120 s, 300 s, 1200 s, and 2400 s in the parent phase (320 K), respectively. The inset shows the electrical resistivity of the sample during the first (without deaging) and the last (after 2400 s deaging) thermal cycles.

to investigate the deaging process, the sample was held in the parent phase state (at 320 K) for 0, 15, 45, 60, 240, 900, and 1200 s sequentially and had no waiting in martensite. As a result, the sample was aged in the parent phase for 0 s, 15 s, 60 s, 120 s, 300 s, 1200 s, and 2400 s, respectively.

The inset of Fig. 1 shows the heating and cooling processes of electrical resistivity of the sample in the first (without deaging) and the last (after 2400 s deaging) thermal cycle. The sharp decrease in specific resistivity during heating processes indicates the reverse MT; and the abrupt increase during the cooling processes indicates the occurrence of MT. It can be seen that  $M_s$  in the first cycle without deaging is 308 K and it decreases to 302 K in the last cycle after full deaging. The plot of  $M_s$  versus time in Fig. 1 clearly shows that the  $M_s$  temperature gradually decreases with deaging time and saturates after 500 s. Thus, the deaging is a process requiring time, and the extent of deaging is insignificant within a short time of parent phase aging (500 s for the present Au-49.5Cd alloy).

The most interesting finding here is that the physical properties of an equilibrium martensitic alloy (e.g.,  $M_s$ ) can be altered during deaging process, which shows a “fast parent phase aging” effect. Furthermore, this time-dependent behavior is a clear signal of atomic diffusion, i.e., the present observed parent phase aging may be related to a kind of atomic diffusion that may be difficult to probe experimentally.

We explored the atomic process involved in the parent phase aging by an *A-B* type B2 model material. As the experimental sample is the nonstoichiometric binary alloy, we introduced 5 at % excess *A* atoms into the  $\beta$  sublattice to replace *B* atoms as the antisite point defects. The model consists of  $48^3$  unit cells and periodic boundary conditions were used in three dimensions. A combination of MD and MC approaches<sup>11</sup> was used to simulate the observed parent phase aging effect. The MD method, based on the Parrinello–Rahman scheme<sup>12</sup> and the isobaric-isothermal ensemble, was applied to simulate the diffusionless martensitic (reverse) transformation; The MC method, based on the classic METROPOLIS algorithm<sup>13</sup> and canonical ensemble, was used to simulate the aging process in the parent phase. A simple 8–4

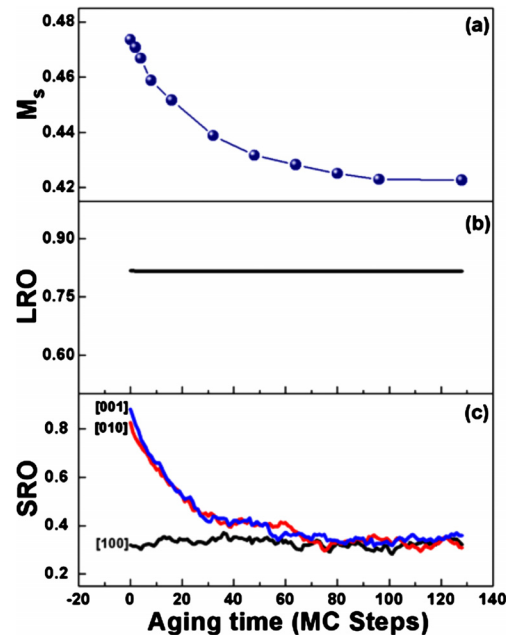


FIG. 2. (Color online) The changes in (a)  $M_s$  temperature, (b) LRO of  $\beta$  sublattice, and (c) SRO of point defects with the aging time (MC step) in the parent phase.

Lennard–Jones potential was employed in both MD and MC simulations,<sup>14</sup> which reproduced well the common features of a generic MT from the B2 parent phase to an orthorhombic based martensite.<sup>14–16</sup>

Similar to the experimental procedure, the well-aged martensitic model system was first heated up to the parent phase (at normalized temperature 0.54), and was then aged at this temperature for different MC steps to obtain a group of “samples” with different aging times. The “samples” were then cooled down to martensite (at normalized temperature 0.34). During the above process the variations in  $M_s$  and LRO of  $\beta$  sublattice with aging time in the parent phase were monitored and the results are shown in Figs. 2(a) and 2(b).

As shown in Fig. 2(a), it is clear that the  $M_s$  temperature decreases with the aging time (MC steps) in the parent phase, which is consistent with our experimental results. Figure 2(b) further shows the evolution of LRO (defined as in Ref. 17) with the aging time (MC steps) in the parent phase. We observe that there is no change in LRO of  $\beta$  sublattice during the aging process in the parent phase. This indicates that there is no change in the average structure during the aging process in the parent phase, which is also consistent with the experimental observation for the present Au-49.5Cd alloy.<sup>7</sup> Thus our atomistic simulations reproduce the observed parent phase aging effect.

We notice that the lack of variation in LRO during aging in the parent phase also indicates that the effective migration of atoms always occurs within one sublattice, not between the two sublattices of the B2 structure. We thus deduce that the short range migration of point defects plays an important role in the parent phase aging. As the short range configuration of point defects can be characterized by the short range order (SRO) parameter of point defects,<sup>11</sup> we further calculate the change in SRO of point defects with the aging time in the parent phase.

Figure 2(c) shows the change in SRO of nearest neighbors along [100], [010], and [001] directions of the  $\beta$  sublattice.

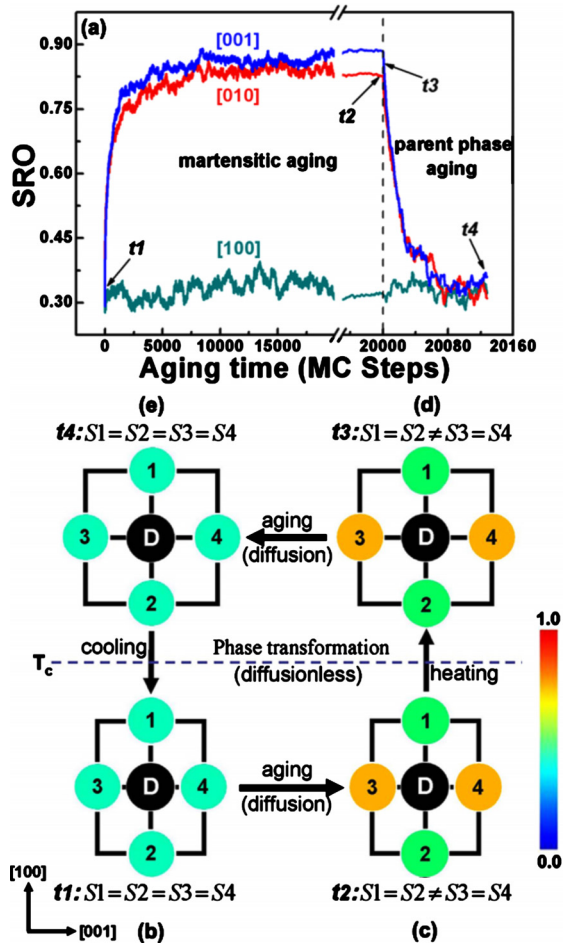


FIG. 3. (Color online) Unified microscopic explanation for both martensite aging effect and the present parent phase aging effect. (a) the changes in defect SROs in nearest neighbors along [100], [010], and [001] directions with aging time (MC step) in the martensite (from Ref. 11) and the parent phase [Fig. 2(c)], in which points  $t_1$ ,  $t_2$ ,  $t_3$ , and  $t_4$  represent fresh martensite, well-aged martensite, fresh parent phase, and well-aged parent phase, respectively. [(b)–(e)] defect SROs in nearest neighbors along [100] and [001] directions (represented by  $S_1$ ,  $S_2$ ,  $S_3$ , and  $S_4$ ) corresponding to points  $t_1$ ,  $t_2$ ,  $t_3$ , and  $t_4$  in Fig. 3(a).

tice with aging time (MC step) in the parent phase. It is clear that the SRO values change with aging in the parent phase. Before aging, the defect SROs in the above three directions are different. However, with increase in aging time in the parent phase, the defect SROs in the above three directions tend to be close to each other and are finally essentially the same. Likewise, we observe that the change in defect SROs with aging in the parent phase is similar to that of  $M_s$  [Fig. 2(a)]. This indicates that the origin of the parent phase aging is closely related to the change in the defect SROs during aging in the parent phase.

Interestingly, the present observed parent phase aging effect and its origin is quite similar to one of the well-known martensite aging effects, i.e., martensitic stabilization.<sup>11</sup> As proved in our previous work,<sup>11</sup> its origin is also closely related to the change in defect SROs during aging in the martensite. These clues indicate that the underlying mechanism for the parent phase aging could be closely related to that of the martensitic stabilization. For martensite stabilization, our

previous study has clarified that they stem from the SC-SRO principle,<sup>6,7,11</sup> which refers to the fact that the symmetry of SRO of point defects in equilibrium should conform to the symmetry of their host lattice.

Combining with our previous work in Ref. 11, we can obtain the evolution of SRO of the nearest neighbors along [100], [010], and [001] directions of  $\beta$  sublattice during a thermal cycle, which contains both martensite aging (data from Ref. 11) and parent phase aging [Fig. 2(c)]. The results are shown in Fig. 3(a). It is clear that the defect SROs along [100], [010], and [001] directions change from equivalence to nonequivalence during the martensite aging, and then revert to equivalence during the parent phase aging. Based on the data of defect SRO in Fig. 3(a), we can further illustrate the defect SROs in the nearest neighbors along [100] and [001] directions in four specific cases [time  $t_1$  to  $t_4$  in Fig. 3(a), only in two-dimension for simplification] in detail, and the results are shown in Figs. 3(b)–3(e).

As Fig. 3(e)  $\rightarrow$  (b)  $\rightarrow$  (c) corresponds to the behavior of martensitic stabilization, and Fig. 3(c)  $\rightarrow$  (d)  $\rightarrow$  (e) refers to the process of parent phase aging effect, it is clear that the SC-SRO principle can provide a unified microscopic explanation for both martensite aging effect and the observed parent phase aging effect. The SC-SRO tendency of point defects provides the driving force for re-establishing SROs of point defects during aging in both martensite and parent phase, and hence results in the changes in physical properties (e.g., transformation temperature) of the SMAs.

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