Shape Memory Effect and Superelasticity in a Strain Glass Alloy

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The shape memory effect and superelasticity are usually found in alloys exhibiting spontaneous martensitic transformation. Thus it is hard to imagine that such interesting effects can appear in a system without a martensitic transformation. In this Letter we show shape memory and the superelasticity effect in a nonmartensitic $Ti_{48.5}Ni_{51.5}$ alloy, which has no martensitic transformation but undergoes a "strain glass" transition. *In situ* x-ray diffraction experiment showed that the shape memory and superelasticity in strain glass stem from a stress-induced strain glass to martensite transformation and its reverse transformation. The new shape memory and superelasticity in strain glass extends the regime of the shape memory effect and superelasticity and may lead to novel applications.

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A class of metallic alloys can memorize a predefined "hot" shape (i.e., shape memory effect) upon heating to above a critical temperature, and can also show a huge pseudoelastic deformation behavior (i.e., superelasticity) when deformed above this temperature. These alloys are known as shape memory alloys and have attracted keen interest over the past decades [1,2] and have found wide applications [1].

So far, the shape memory effect and superelasticity in a metallic system are known to originate from a diffusionless structural transformation called martensitic transformation, in which below a transformation temperature the cubic unit cells of the parent phase spontaneously undergo the same distortion over very long range (called long-range ordering of the strains) and hence form a distorted lattice called martensite [3–5]. In a martensitic state, different combinations of the low-symmetry martensite "variants" can results in various macroscopic "cold" shapes. Upon heating up to above the transformation temperature, all the martensite variants revert to the undistorted parent phase [1] and hence recover the original hot shape of the parent phase. This is the shape memory effect. In a parent state, stress loading and unloading above the martensitic transformation temperature can induce a transformation from the cubic parent lattice to a martensite lattice and then back to the cubic lattice; thus very large recoverable strain is generated in this process. This is the superelasticity. Apparently the shape memory effect and superelasticity rely on the existence of a spontaneous martensitic transformation, and it is hard to imagine an alloy without showing martensitic transformation can exhibit these two remarkable properties. Here we report an unexpected shape memory effect and superelasticity in a "nonmartensitic" alloy $Ti_{48.5}Ni_{51.5}$ (in a single phase $B2$ state), which has been found recently to undergo a "strain glass transition" [6], a transition with no change in average structure.

A strain glass alloy can be considered as a derivative of a martensitic system but without showing martensitic transformation. It is formed through doping point defects (excess solute atoms or alloying elements) into a martensitic alloy to destroy the long-range strain order. As the result, martensitic transformation is suppressed, but local strain order still exists and is frozen below a freezing temperature [6]. The disappearance of martensitic transformation by doping has been well observed previously [7–10], but it was not until very recently that such "nontransforming systems" have been identified as strain glasses [6]. Figure 1 shows the typical features of a strain glass alloy $Ti_{48.5}Ni_{51.5}$ (obtained by a 1273 K solution treatment and followed by water quenching [6]), which is obtained by doping 1.5 at. % excess Ni into a martensitic stoichiometric compound $Ti_{50}Ni_{50}$. Previous studies [8,9] have shown that $Ti_{48.5}Ni_{51.5}$ exhibits no martensitic transformation down to 4.2 K. Confirming this conclusion, our x-ray diffraction (XRD) investigation over a wide temperature range from 373 to 108 K shows it keeps a $B2$ structure of parent phase over the entire temperature range, as depicted in Fig. 1(a). However, being different from a conventional "dead" nontransforming alloy, which would show no anomaly at any temperature, strain glass $Ti_{48.5}Ni_{51.5}$ shows a strain glass transition from dynamically disordered local strains (unfrozen strain glass) into frozen locally ordered strains (frozen strain glass), as shown in the insets of Fig. 1(b). This is manifested by the appearance of a frequency-dependent dip in the ac elastic modulus at the freezing temperature $T_g(\omega)$ and a corresponding peak in the internal friction $\tan\delta$, as shown in Fig. 1(b). Its "ideal" freezing temperature T_0 (T_g at 0 Hz) is 160 K, which can be obtained by fitting the frequency (ω) dependence of $T_g(\omega)$ with the Vogel-Fulcher relation [6] $\omega = \omega_0 \exp[-E_a/k_B(T_g - T_0)]$. The locally ordered strain domains have been imaged with high-resolution transmission electron microscopy, and they have been found to yield diffuse scattering in electron diffraction [6]. It should be noted here that the strain glass is fundamentally different

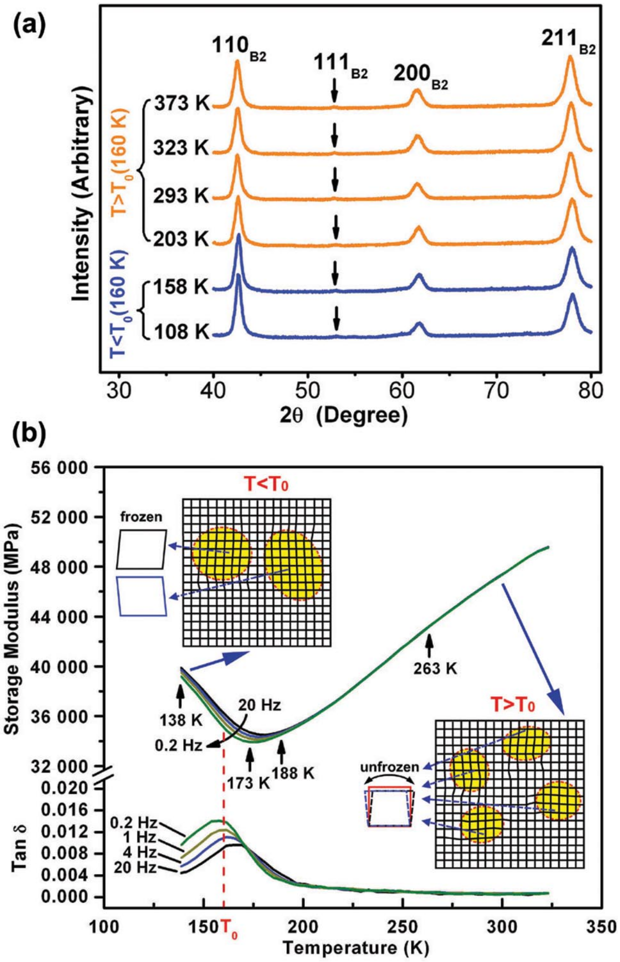

FIG. 1 (color). Key features of strain glass as exemplified by $Ti_{48.5}Ni_{51.5}$. $T_0(= 160\ K)$ is the ideal freezing temperature. (a) X-ray diffraction indicates that the absence of a change in average structure at T_0, and this alloy keeps a $B2$ structure down to the lowest attainable temperature (108 K). (b) Dynamic mechanical measurement, however, shows an anomalous, frequency-dependent modulus dip around T_0 and a corresponding internal friction peak at a lower temperature. The insets in (b) show schematically the microscopic picture of the strain freezing process.

from the well-observed premartensitic tweed [11], because first, the former one does not transform spontaneously into normal martensite whereas the latter one does, and second and the most important, the strain glass is formed by a phase transition (glass transition) but the precursory tweed is not [6]. It should be stressed that although the local symmetry of strain glass is lower than cubic, the average lattice keeps a "$B2$ cubic" structure at any temperature. Therefore, this "cubic" phase should be considered as a "pseudocubic" because the local symmetry is lower than cubic.

Now we show that this nonmartensitic, strain glass $Ti_{48.5}Ni_{51.5}$ exhibits shape memory and superelasticity. Figure 2(a) shows the deformation behavior of this alloy below T_0 (at 138 K) and above T_0 (at 173, 188, and 263 K). When deformed at 138 K ($< T_0$), the sample showed a very large plastic deformation ($\sim 8.1\%$) at a surprisingly low stress (~ 200 MPa) for such a hard intermetallic compound. Interestingly, this permanent deformation gradually disappeared (marked by the dashed line) on heating to above T_0; i.e., the sample memorizes its original shape. This is clearly a shape memory effect. Figure 2(b) shows visual evidence for the shape memory effect of a $Ti_{48.5}Ni_{51.5}$ strain glass wire. The plastically deformed straight specimen at 138 K recovered its original straight shape upon heating to 173 K ($> T_0$). When deformed at a temperature above T_0, the strain glass alloy showed an interesting "superelastic" behavior, contrasting the plastic deformation behavior below T_0, unexpected for a nonmartensitic alloy. As shown in Fig. 2(a), at 173 K ($= T_0 + 13$ K), the sample demonstrated a large recoverable strain of 7.5%; this is a superelasticity of strain glass. At a higher temperature of 188 K, the sample showed similar superelastic behavior with a higher critical stress. As the maximum applied stress for our experimental setup was restricted to 280 MPa, the superelastic strain (2.2%) at 188 K did not reach the saturation value. At 263 K ($\gg T_0$), 280 MPa stress is not sufficient to induce a superelastic behavior, so the sample exhibited only a linear elastic deformation behavior. Figure 2(c) provides visual evidence for the superelasticity of the strain glass $Ti_{48.5}Ni_{51.5}$. At 173 K, a straight specimen was first severely bent but it recovered its original straight shape immediately upon unloading.

To understand the microscopic mechanism underlying these effects in strain glass, we performed an *in situ* XRD experiment to monitor the possible structure change during the shape memory and superelasticity processes, respectively. Figure 3(a) shows the structure change of a strain glass alloy $Ti_{48.5}Ni_{51.5}$ during a "shape memory process." When the specimen was cooled to 138 K ($< T_0$) under zero stress, diffraction pattern [Fig. 3(a)] showed "pseudo-$B2$" structure as shown in Fig. 1(a). As the stress increased to about 200 MPa [the "plateau stress" in the stress-strain curve for 138 K in Fig. 2(a)], the intensity of the $B2$ peak decreased and some new peaks appeared, which were fully indexed as a commonly observed $B19'$ martensite in Ti-Ni alloys [12]. When the stress reaches 280 MPa [the maximum stress point for the 138 K curve in Fig. 2(a)], the $B2$ peak disappeared and the intensity of $B19'$ peaks reached a maximum. Moreover, the $B19'$ peaks remained essentially unchanged when the stress was back to zero, which suggests the $B19'$ martensitic state is stable even after unloading. When the sample was heated to 195 K ($> T_0$), $B19'$ peaks disappeared and the "$B2$" pattern reappeared; this corresponds to the shape recovery or memory of the sample during heating up to above T_0. Therefore, the *in situ* XRD experiment demonstrates that the plastic deformation of the strain glass corresponds to a stress-induced transition from the pseudo-$B2$ strain glass to

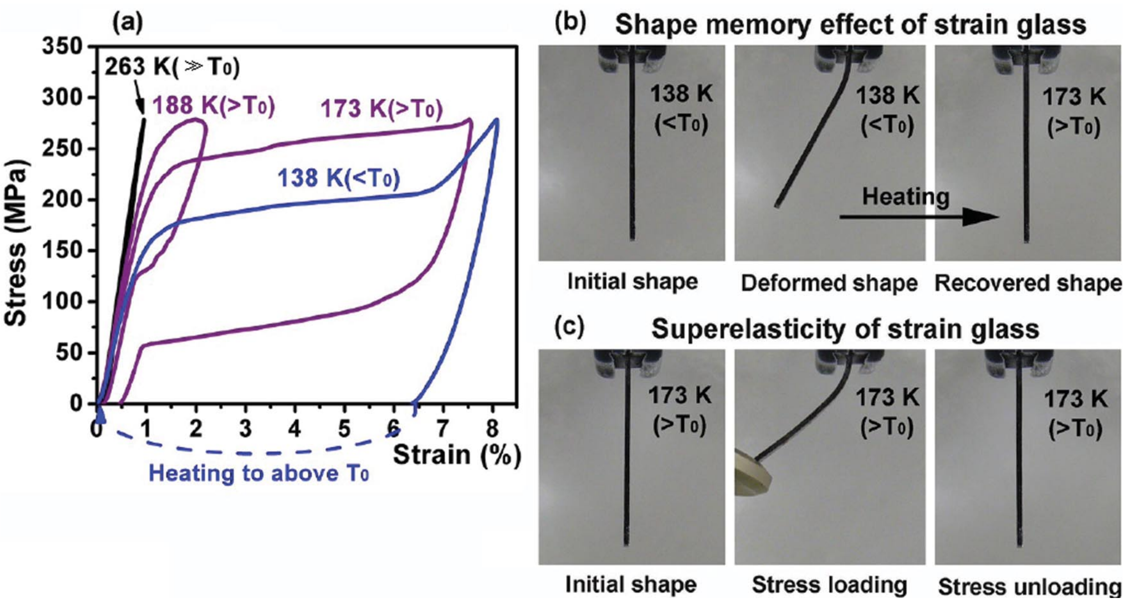

FIG. 2 (color). The shape memory effect and superelasticity of strain glass alloy Ti$_{48.5}$Ni$_{51.5}$. (a) The stress-strain curves over a wide temperature range spanning the ideal freezing temperature $T_0 (= 160$ K) of strain glass transition. (b) and (c) show visual evidence for shape memory effect and superelasticity, respectively.

a $B19'$ martensite, and the heating-induced shape recovery or memory stems from a transformation from a stress-induced $B19'$ martensite into an unfrozen strain glass (at $T > T_0$). Clearly this microscopic process is fundamentally different from that of a martensitic Ti-Ni alloy, in which the plastic deformation is due to a twinning process (martensite variant switching) of martensite and the shape recovery is due to a reverse martensitic transformation.

Figure 3(b) shows the structure change of the strain glass Ti$_{48.5}$Ni$_{51.5}$ during a "superelastic process." At 173 K ($= T_0 + 13$ K), the sample showed a cubic $B2$ diffraction pattern, as expected for strain glass. When applied with a stress of 250 MPa, many $B19'$ martensite peaks appeared and the $B2$ peak was weakened. This indicates that martensite was induced from the pseudo-$B2$ unfrozen strain glass, which corresponds to the stress plateau for the 173 K curve in Fig. 2(a). When the stress reached 280 MPa, the $B2$ reflection vanished, indicating the unfrozen strain glass transformed completely into the $B19'$ martensite. Upon stress unloading, the $B19'$ martensite reflections gradually disappeared and the $B2$ reflection reappeared, suggesting that the stress-induced martensite transformed back to the pseudo-$B2$ unfrozen glassy state. Therefore, the superelasticity of strain glass above T_0 is attributed to a stress-induced reversible transformation from unfrozen strain glass state to the $B19'$ martensite. It should be noted that the superelasticity of strain glass has a significant difference from that of a martensitic alloy. For a martensitic alloy, the existence of superelasticity or stress-induced transformation is determined *a priori* by the existence of a spontaneous, temperature-induced martensitic transformation from a thermodynamic viewpoint. However, for strain glass there exists no spontaneous martensitic transformation, yet martensite can by induced by stress. This is quite unusual.

The origin of the shape memory effect and superelasticity in strain glass may be explained in a phenomenological way as follows. As strain glass is a derivative of martensite through doping point defects, it is conceivable

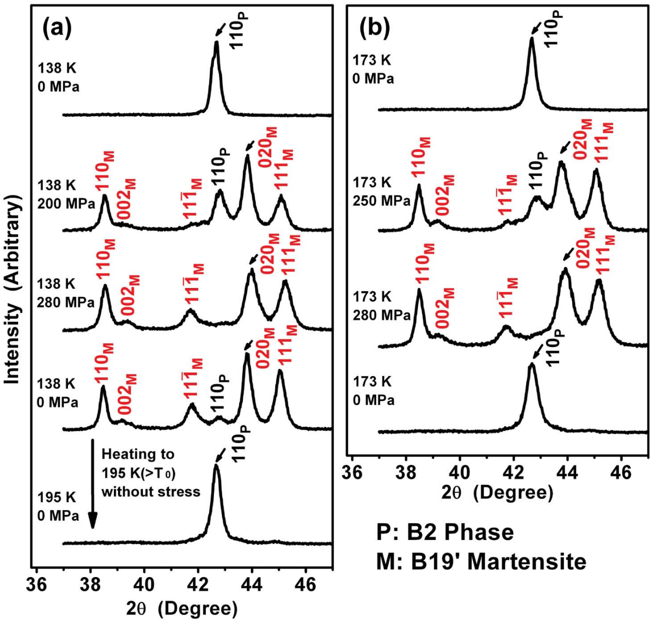

FIG. 3 (color). *In situ* x-ray diffraction evidence for a structure change during (a) a shape memory process [tensile loading at 138 K ($< T_0$) and followed by heating to 195 K ($> T_0$)], and (b) a superelasticity process [tensile loading at 173 K ($> T_0$) and followed by unloading].

that the strain glass $\mathrm{Ti}_{48.5}\mathrm{Ni}_{51.5}$ shares a similar free energy landscape of a normal Ti-Ni martensitic alloy [4,5,13,14] where the long-range strain-ordered $B19'$ state is a thermodynamic stable state at low temperature but metastable at high temperature. However, the point defects (excess Ni atoms here) in the system create nearly equal, local energy minima in the free energy landscape and thus cause frustration in the system. Analogous to case of a spin glass [15], the system cannot undergo a long-range strain ordering transition into $B19'$ martensite even down to 0 K, although $B19'$ martensite is the thermodynamically stable state. Instead, the system undergoes a ''freezing transition'' of strains at T_0, below which local strains are frozen, which is the observed strain glass transition. This picture is consistent with the physically parallel glass phenomenon—ferroelectric relaxor [16,17], where only locally ordered polar nanodomains exist.

When an external stress is applied to the frozen strain glass state well below T_0, long-range strain ordering (i.e., $B19'$ martensite) can be induced, because the external stress assists the system to overcome the local barriers. Since the $B19'$ martensitic state has the lowest ground energy far below T_0, it is stable even after withdrawing external stress. This explains the observed plastic deformation of strain glass. When the stress-induced $B19'$ martensite is heated to $T > T_0$, it becomes metastable and tends to transform into the unfrozen glassy state. At such high temperature, this transition is kinetically possible because the enhanced thermal activation is enough to overcome local barriers; thus we observe a recovery of the plastic strain upon heating, i.e., shape memory effect of strain glass. On the other hand, if the unfrozen glass state (above T_0) is stressed, $B19'$ martensite can also be induced, because stress can stabilize certain martensite variants. Moreover, the induced $B19'$ martensite becomes unstable after stress unloading, so the system reverts to the original unfrozen glassy state again. This stress-induced unfrozen glass to $B19'$ transformation is the origin of the observed superelasticity.

We have shown in the above that the shape memory effect and superelasticity of strain glass are due to a stress-induced transformation from strain glass to long-range strain-ordered martensite. Interestingly, a physically parallel phenomenon has been found in ferroelectric relaxor [18,19], in which long-range electrical dipolar order can also be induced from a glassy relaxor state by applying an external dc electrical field. Combining these parallel facts, it appears that field-induced transition from glass to a long-range-ordered state is a quite general phenomenon in glass systems. On the other hand, as the strain glass and the associated new shape memory effect result from the effect of point defects, our work demonstrates the important role of point defects in transforming systems, which has been shown to generate other exotic effects [20–22].

In conclusion, we discovered a new kind of shape memory effect and superelasticity in a nonmartensitic, strain glass system. Well below the ideal freezing temperature T_0 of strain glass transition, stress can induce a strain glass to $B19'$ martensite transformation and causes a large plastic strain. Upon heating, the induced $B19'$ martensite transforms into an unfrozen strain glass and causes a recovery to the original shape. Above T_0, stress causes a reversible stress-induced transformation from an unfrozen strain glass to $B19'$ martensite. The new shape memory effect and superelasticity in nonmartensitic, strain glass alloy may significantly expand the regime of shape memory and superelasticity and may provide possibilities for applications.

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[1] *Shape Memory Materials*, edited by K. Otsuka and C. M. Wayman (Cambridge University Press, Cambridge, 1998).
[2] J. W. Christian, *The Theory of Transformations in Metals and Alloys* (Pergamon, London, 2002).
[3] A. G. Khachaturyan, *Theory of Structural Transformation in Solid* (Wiley, New York, 1983).
[4] E. K. H. Salje, *Phase Transformation in Ferroelastic and Co-elastic Crystal* (Cambridge University Press, Cambridge, 1993).
[5] A. Planes and L. Mañosa, Solid State Phys. **55**, 159 (2001).
[6] S. Sarkar, X. Ren, and K. Otsuka, Phys. Rev. Lett. **95**, 205702 (2005).
[7] T. Honma and H. Takei, J. Jpn. Inst. Met. **39**, 175 (1975).
[8] T. Kakeshita, T. Fukuda, H. Tetsukawa, T. Saburi, and K. Kindo, Jpn. J. Appl. Phys. **37**, 2535 (1998).
[9] C. Somsen *et al.*, Mater. Sci. Eng. A **237–275**, 310 (1999).
[10] M. S. Choi *et al.*, Philos. Mag. **86**, 67 (2006).
[11] D. Schryvers and L. Tanner, Ultramicroscopy **32**, 241 (1990).
[12] Y. Kudoh *et al.*, Acta Metall. **33**, 2049 (1985).
[13] F. Falk, Acta Metall. **28**, 1773 (1980).
[14] G. R. Barsch and J. A. Krumhansl, Phys. Rev. Lett. **53**, 1069 (1984).
[15] J. A. Mydosh, *Spin Glasses* (Taylor & Francis, London, 1993).
[16] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
[17] G. A. Samara, J. Phys. Condens. Matter **15**, R367 (2003).
[18] R. Sommer, N. K. Yushin, and J. J. van der Klink, Phys. Rev. B **48**, 13 230 (1993).
[19] J. L. Dellis *et al.*, Ferroelectrics **201**, 167 (1997).
[20] X. Ren and K. Otsuka, Nature (London) **389**, 579 (1997).
[21] X. Ren and K. Otsuka, Phys. Rev. Lett. **85**, 1016 (2000).
[22] X. Ren, Nat. Mater. **3**, 91 (2004).