

High temperature strain glass in $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ alloy and the associated shape memory effect and superelasticity

Yumei Zhou,^{1,2,3} Dezhen Xue,^{1,2,3} Xiangdong Ding,^{1,2} Kazuhiro Otsuka,^{3,1} Jun Sun,^{2,1} and Xiaobing Ren^{3,1,a)}

¹Multi-Disciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

²State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

³Ferroc Physics Group, National Institute for Materials Science, Tsukuba, 305-0047 Ibaraki, Japan

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Strain glass has recently been reported in $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) alloys and caused by the existence of point defects. This strain glass alloy, being nonmartensitic, exhibits shape memory effect (SME) and superelasticity (SE) around the freezing temperature T_0 . However, the T_0 of $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) strain glass alloy is very low (~ 160 K), thus restricting its potential applications. In the present letter, we report a strain glass system, $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ ($x \geq 9$ at %), which has a significantly higher freezing temperature. It is based on a high-temperature martensitic system TiPd (with $M_s \sim 810$ K) and dopant Cr (as point defect). For $\text{Ti}_{50}(\text{Pd}_{40}\text{Cr}_{10})$ strain glass, the freezing transition occurs at $T_0 \sim 250$ K, being close to the room temperature. Correspondingly, it exhibits SME and SE around its high T_0 . We further clarified that T_0 of strain glass alloy is controlled by the martensitic transformation temperature M_s (i.e., martensite stability) of its corresponding host alloy without point defect. Our work provides insight into how to develop strain glass with desired T_0 and the associated SME and SE for applications. © 2009 American Institute of Physics. [doi:10.1063/1.3249580]

Glass transition has been observed in a wide range of complex systems and it usually occurs due to the existence of randomness, which causes frustration in the system so that the long-range ordering becomes inaccessible.^{1,2} Recently, strain glass, a glassy state in ferroelastic/martensitic systems (where lattice strain is the order parameter), is reported to exist in $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) alloys. This class of glass is formed through doping sufficient point defects (excess solute atoms or alloying elements) into a normal martensitic system.³ The competing interaction between randomly distributed local stresses produced by the random point defects suppresses the long-range strain ordering toward a normal martensite phase. As a result, the system freezes into a strain glass state, in which only nanosized martensitelike domains with local strain ordering exist. Hence, strain glass is derived from the normal martensitic system and it is physically parallel to relaxor ferroelectrics^{4,5} and cluster spin glass,⁶⁻⁹ which are the glassy states derived from normal ferroelectric system and ferromagnetic system, respectively.

For decades shape memory effect (SME) and superelasticity (SE) have been known to be characteristic of the systems exhibiting martensitic transformation.¹⁰⁻¹⁴ Interestingly, recent study shows that the above $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) strain glass alloy also exhibits SME and SE around its freezing temperature T_0 . Such SME and SE stem from a different mechanism, i.e., stress-induced strain glass to long-range-strain-ordered martensite transition.¹⁵ This result expands the regime of SME and SE to nonmartensitic, strain glass alloys. Nevertheless, $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) strain glass alloy has a very low T_0 (~ 160 K), which limits its potential for practical applications. Thus, it is of funda-

mental interest and technical importance to search for strain glass with high T_0 in ferroelastic/martensitic systems. In this letter, we show that $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ ($x \geq 9$ at %) alloy undergoes a strain glass transition with significantly high T_0 around the room temperature; it also shows the SME and SE around its high T_0 . We further show that its high T_0 is due to the high martensitic transformation temperature (M_s) of its corresponding undoped host alloy (TiPd).

$\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ alloys with Cr concentration of $x=5, 7, 8, 9, 10, 11,$ and 12 at % were tested in our study. Cr is designed to substitute for Pd and acts as point defect. Hereafter these alloys are abbreviated as 5Cr, 7Cr, 8Cr, 9Cr, 10Cr, 11Cr, and 12Cr, respectively. Base ingots were made by induction melting 99.9% pure Ti, 99.9% pure Pd and 99.9% pure Cr in argon atmosphere. The specimens were solution-treated at 1373 K for 1 h in evacuated quartz tubes, followed by water quenching. DSC (differential scanning calorimetry) measurement was done to determine the martensitic transformation temperature and latent heat. Multifrequency dynamical mechanical analysis (DMA) measurement was carried out to test the possible strain glass transition. Specimens were measured in a single cantilever mode with constant displacement amplitude of $15 \mu\text{m}$. The elastic modulus and internal friction values were recorded for six frequencies (0.2/0.4/1/4/10/20 Hz) as a function of temperature; the cooling and heating rate was 2 K/min. *In situ* XRD (x-ray diffraction) technique from high temperature to low temperature was used to identify the possible structural change.

As mentioned above, the formation of strain glass is due to the existence of point defects, which suppresses the formation of long-range-strain-ordered martensite phase.³ Thus, we first explore the effect of defect doping on the martensitic transformation behavior of these $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ alloys by

^{a)}Electronic mail: ren.xiaobing@nims.go.jp.

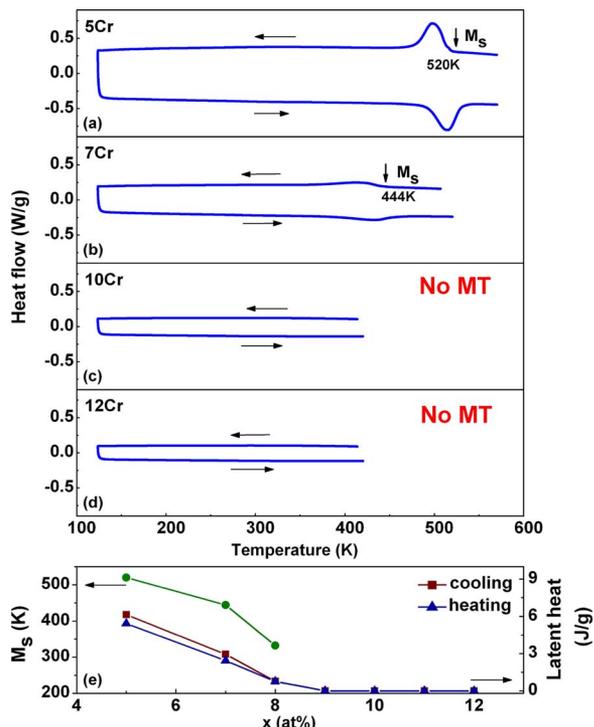


FIG. 1. (Color online) Transformation behavior of Cr doped $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ ($x=5,7,8, 9, 10,11,$ and 12 at %) alloys by DSC measurement. *MT* represents the normal martensitic transformation.

comparing the DSC results shown in Fig. 1. The exothermal/endothermic peaks and big hysteresis (~ 15 K) in Figs. 1(a) and 1(b) suggest that both 5Cr and 7Cr undergo a normal martensitic transformation, which was identified to be $B2$ - $B19$ by XRD. It was noted that, Cr doping dramatically decreases the onset temperature of normal martensitic transformation (M_s) and the transformation latent heat, as shown in Fig. 1(e). Interestingly, for alloys with Cr concentration more than ~ 9 at % [Fig. 1(c) and 1(d)], DSC peak virtually vanishes, suggesting the absence of normal martensitic transformation, which is further confirmed by the *in situ* XRD results showing no peak splitting in the following. Such evolution of transformation behavior as a function of defect (Cr here) concentration is similar with that of Ni-rich Ti-Ni system.^{3,16}

We then show that those seemingly “nontransforming” alloys, 9Cr, 10Cr, 11Cr, and 12Cr, actually undergo a strain glass transition. Strain glass transition is characterized by two essential glass signatures.¹⁷ One is the frequency dispersion of the AC mechanical properties (elastic modulus/internal friction), which obeys a Vogel–Fulcher relation $\omega = \omega_0 \exp[-E_a/k_B(T_g - T_0)]$;⁷ this behavior reflects a dynamic freezing transition. The other is the invariance in the average structure, reflecting the absence of long-range strain ordering during such a transition. Figure 2(a) shows the first signature of strain glass for 10Cr, measured by DMA. The elastic modulus shows a frequency-dependent dip at a critical temperature (glass transition temperature T_g) and the internal friction shows a frequency-dependent peak at temperature lower than T_g . The frequency dependence of $T_g(\omega)$ follows the Vogel–Fulcher relation, as shown in the inset of Fig. 2(a). The fitting yields a freezing temperature T_0 (T_g at 0 Hz) of 250 K. The second signature is shown in (b1), (b2), and (b3) of Fig. 2, that is the average cubic ($B2$) structure remains

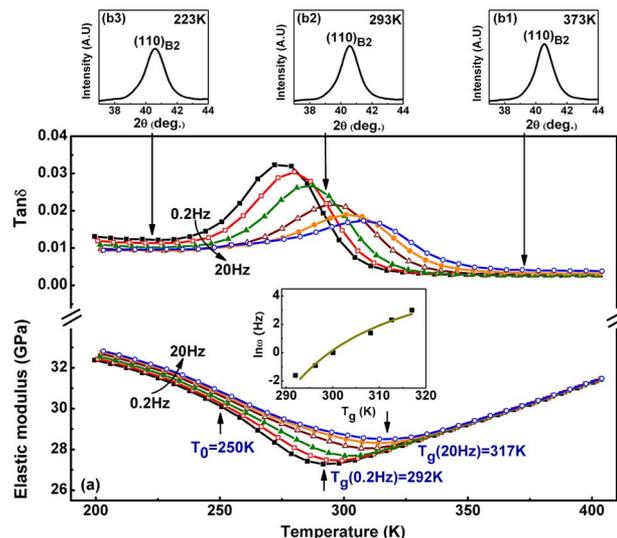


FIG. 2. (Color online) Evidence for strain glass transition in $\text{Ti}_{50}(\text{Pd}_{40}\text{Cr}_{10})$ alloy. DMA results in (a) demonstrate that it undergoes a dynamic freezing transition, which is manifested by the strong frequency dispersion of the elastic modulus dip temperature T_g and internal friction peak temperature. Inset of (a) shows fitting of $T_g(\omega)$ using Vogel–Fulcher relation $\omega = \omega_0 \exp[-E_a/k_B(T_g - T_0)]$ (Ref. 7), where the freezing temperature $T_0 = 250$ K. *In situ* XRD results in (b1), (b2), and (b3) show that there is no change in the average structure and the $B2$ cubic structure is kept to lower than T_0 . The above two features characterize the strain glass transition.

unchanged during the freezing transition, because there is no peak splitting throughout a wide temperature range (223 K–373 K) spanning the above freezing temperature T_g . Therefore, 10Cr undergoes a strain glass transition due to the sufficient doping of point defects. The similar strain glass signatures have also been confirmed at higher Cr doping ($x > 10$ at %), but with a lower freezing temperature T_0 , seen in Fig. 4.

It should be noted that 10Cr strain glass alloy has a freezing temperature $T_0 \sim 250$ K, which is much higher than that of $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) strain glass ($T_0 \sim 160$ K). It is of interest to explore whether 10Cr strain glass alloy can exhibit similar SME and SE around its higher T_0 . Figure 3(a) shows that a 10Cr strain glass wire can be plastically deformed in the frozen strain glass state (243 K = $T_0 - 7$ K), but it can recover to the initial shape during heating to above T_0 (263 K = $T_0 + 13$ K). This is the SME. Figure 3(b) demonstrates a superelastic behavior of a 10Cr strain glass wire in its unfrozen glass state (293 K = $T_0 + 43$ K), where a large deformation recovers immediately upon unloading. The most notable feature of the present 10Cr strain glass as compared with a typical $\text{Ti}_{50-x}\text{Ni}_{50+x}$ strain glass ($\text{Ti}_{48.5}\text{Ni}_{51.5}$) is that the SME and SE of the former appears at a much higher temperature range, as shown in Fig. 3(c). Clearly, 10Cr strain glass shows SE around the ambient temperature range of 250–325 K, and SME over the temperature range of 215–250 K. By contrast, $\text{Ti}_{48.5}\text{Ni}_{51.5}$ strain glass shows SE and SME at much lower temperature range (< 200 K). Therefore, 10Cr strain glass alloy shows the similar SME and SE around its high T_0 with that of $\text{Ti}_{50-x}\text{Ni}_{50+x}$ strain glass, but at much higher temperatures.

Now the key question is: why does $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ ($x \geq 9$ at %) strain glass have a high freezing temperature T_0 , whereas $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) strain glass has a low

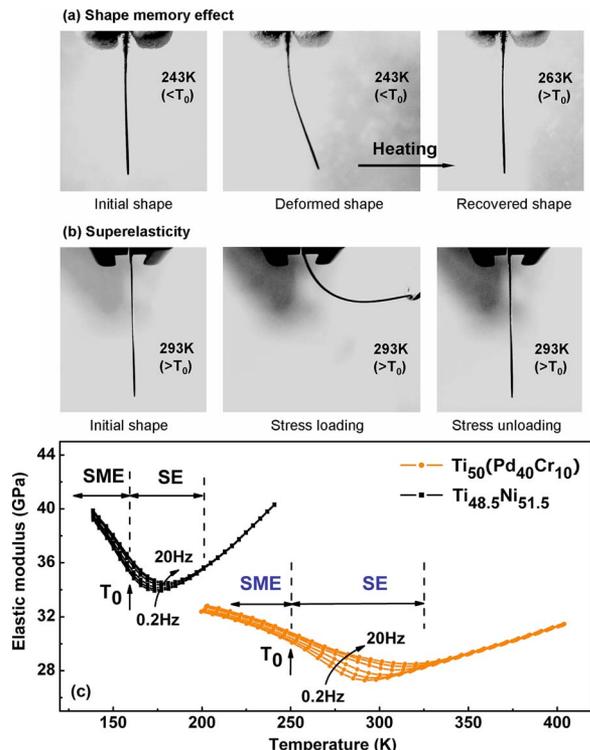


FIG. 3. (Color online) Visual evidence for the SME (a) and SE (b) in strain glass alloy $\text{Ti}_{50}(\text{Pd}_{40}\text{Cr}_{10})$. (c) Comparison of the temperature range for SME and SE between $\text{Ti}_{50}(\text{Pd}_{40}\text{Cr}_{10})$ and $\text{Ti}_{48.5}\text{Ni}_{51.5}$ (Ref. 15) strain glass alloys.

T_0 ? Figure 4 shows that the transformation behavior as a function of defect concentration x is very similar for $\text{Ti}_{50-x}\text{Ni}_{50+x}$ and $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ systems. Below a critical defect concentration, increasing defect concentration only lowers the normal martensitic transformation temperature M_s ; while above this critical defect concentration, the normal martensitic transformation vanishes and is replaced by a strain glass transition. However, there is a clear difference between the two systems. $\text{Ti}_{50-x}\text{Ni}_{50+x}$ starts from a low M_s (~ 335 K) in the pure TiNi host alloy, but $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ starts from a much higher M_s (~ 810 K) in the pure TiPd

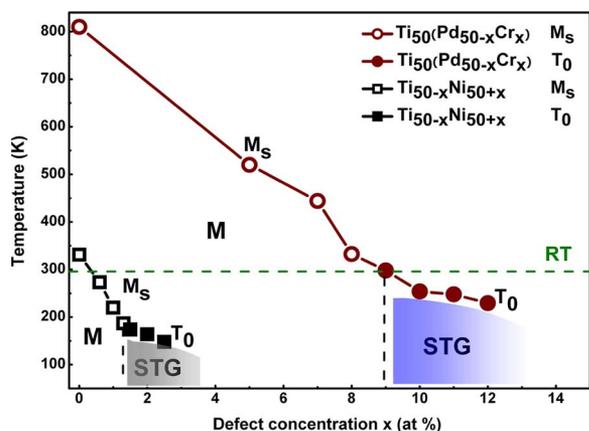


FIG. 4. (Color online) Comparison of transformation behavior as a function of defect concentration between Ni-rich $\text{Ti}_{50-x}\text{Ni}_{50+x}$ alloys (Ref. 16) and Cr doped $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ alloys. M represents martensite phase and M_s is the starting temperature of martensitic transformation; STG represents strain glass phase and T_0 is the freezing temperature of strain glass transition. x is the concentration of point defects (excess Ni or Cr). RT represents the room temperature (~ 298 K).

host alloy. Correspondingly, the former system ends up with a strain glass with low T_0 and the latter system ends up with a strain glass with much higher T_0 . Such a correspondence suggests that T_0 of strain glass alloy seems to be controlled by M_s of the pure host alloy. The reason is given below. High M_s for the pure TiPd alloy indicates that it has high martensite stability, i.e., large thermodynamic driving force for the formation of martensite phase. This ensures that the martensitelike nanodomains in $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ ($x \geq 9$ at %) strain glass can be easily formed at a relatively high temperature, and thus they are frozen at a high T_0 by frustration. In contrast, pure TiNi alloy with low M_s has much lower martensite stability, i.e., much smaller thermodynamic driving force for the formation of martensite phase. As a result, the nanodomains in $\text{Ti}_{50-x}\text{Ni}_{50+x}$ ($x \geq 1.5$ at %) strain glass can be formed only at a lower temperature, and thus can be frozen only at an even lower T_0 . The relationship between M_s of the pure host alloy and T_0 of the corresponding strain glass alloy suggests an important rule for designing the glass transition temperature of strain glasses: high T_0 can be obtained by doping point defects into a host alloy with high M_s , i.e., high martensite stability.

To summarize, with doping sufficient Cr into $\text{Ti}_{50}(\text{Pd}_{50-x}\text{Cr}_x)$ ($x \geq 9$ at %) alloy, the normal martensitic transformation is completely suppressed and a strain glass transition with high freezing temperature T_0 (close to the room temperature) occurs. This high temperature strain glass alloy exhibits SME and SE around the ambient temperature, much higher than that of TiNi-based strain glasses. Finally, we show that T_0 of strain glass alloy is controlled by the martensitic transformation temperature M_s (i.e., martensitic stability) of its corresponding undoped host alloy. This may provide a guideline for designing strain glass with desired T_0 and achieving SME and SE at desired temperatures.

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- ¹K. Binder, *Glassy Materials and Disordered Solids* (World Scientific, London, 2005).
- ²C. A. Angell, *Science* **267**, 1924 (1995).
- ³S. Sarkar, X. Ren, and K. Otsuka, *Phys. Rev. Lett.* **95**, 205702 (2005).
- ⁴B. E. Vugmeister and M. D. Glinchuk, *Rev. Mod. Phys.* **62**, 993 (1990).
- ⁵G. A. Samara, *J. Phys.: Condens. Matter* **15**, R367 (2003).
- ⁶D. Sherrington and S. Kirkpatrick, *Phys. Rev. Lett.* **35**, 1792 (1975).
- ⁷J. A. Mydosh, *Spin Glasses* (Taylor & Francis, London, 1993).
- ⁸K. H. Fischer and J. A. Hertz, *Spin Glasses* (Cambridge University Press, Cambridge, 1991).
- ⁹K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986).
- ¹⁰*Shape Memory Materials*, edited by K. Otsuka and C. M. Wayman (Cambridge University Press, Cambridge, 1998).
- ¹¹A. G. Khachatryan, *Theory of Structural Transformation in Solid* (Wiley, New York, 1983).
- ¹²E. K. H. Salje, *Phase Transformation in Ferroelastic and Co-elastic Crystal* (Cambridge University Press, Cambridge, 1993).
- ¹³J. C. Lashley, S. M. Shapiro, B. L. Winn, C. P. Opeil, M. E. Manley, A. Alatas, W. Ratcliff, T. Park, R. A. Fisher, B. Mihaile, P. Riseborough, E. K. H. Salje, and J. L. Smith, *Phys. Rev. Lett.* **101**, 135703 (2008).
- ¹⁴A. Planes, L. Manosa, and M. Acet, *J. Phys.: Condens. Matter* **21**, 233201 (2009).
- ¹⁵Y. Wang, X. Ren, and K. Otsuka, *Phys. Rev. Lett.* **97**, 225703 (2006).
- ¹⁶Z. Zhang and X. Ren (unpublished).
- ¹⁷Y. Wang, X. Ren, K. Otsuka, and A. Saxena, *Acta Mater.* **56**, 2885 (2008).