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Superelastic behavior and microstructure of Ti19Nb9Zr1Mo (at%) alloy

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ABSTRACT

This letter reports a new strain glass, Ti–19Nb–9Zr–1Mo, exhibiting a combination of good superelasticity of ~3.1% strain after unloading from ~3.5% strain and complete shape memory effect at room temperature. An effect of doping point defect with Mo suppresses the formation of long range strain order's martensites. This doping effect leads to the formation of nanodomains with α'' martensites in microstructure. The superelasticity relates to a random distributed point defect which opposes to the formation of favorable single variant in the alloy.

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1. Introduction

Nickel titanium (NiTi) alloy has been widely used for bone replacements and implants [1] as it exhibited superelasticity near body temperature (~37 °C) which eases the 'stress shielding' problem [2]. However, nickel (Ni) ions released from this alloy might cause serious health problem. Hence, development of non-toxic superelastic alloys have been aroused a lot of attention in replacing NiTi owing to their low modulus [3] and superelasticity of ~3% [4].

Recently, a new non-martensitic superelastic alloy, namely strain glass was reported [5]. It should be reminded that both the shape memory effect (SME) and superelasticity (SE) originate from a thermoelastic martensitic transformation. In contrast, the strain glass has no and/or a minor thermoelastic martensitic transformation but mainly undergoes a strain glass transition. In fact, it is formed through doping point defects, i.e. excess solute atoms or alloying element, into an alloy to destroy the long-range strain order of martensites. As a result, martensitic transformation is suppressed while the local strain order still exists. Therefore, stress/strain loading and unloading even below the martensitic transformation temperature can still induce a transformation from the austenite to a martensite lattices and then back to the austenite lattice. In other words, SME and/or SE could still be

generated without showing the existence of a spontaneous martensitic transformation. Here, we report a new strain glass with a nominal composition of Ti–19Nb–9Zr–1Mo (at%) suitable for biomedical applications. This strain glass exhibits a combination of good superelasticity of ~3.1% strain after unloading from 3.5% strain and complete SME at room temperature.

2. Experimental

Ti–19Nb–9Zr and Ti–19Nb–9Zr–1Mo (at%) alloys were prepared using an argon arc melting technique. The ingot was ~80 g in weight and cold rolled to a plate of 1 mm in thickness with a final cold working ratio of ~90%. All specimens were wire cut from the plate and then annealed at 600 °C for 30 minutes in Ar atmosphere, followed by water quenching to room temperature. Hereinafter, as-annealed Ti–19Nb–9Zr and Ti–19Nb–9Zr–1Mo are abbreviated to TN9Z and TN9ZM, respectively. Phase transformation temperatures of all alloys were determined between –50 °C and 600 °C using the Perkin Elmer (PE) Differential Scanning Calorimetry (DSC7). The crystallographic structures were identified using the Philips X'pert MRD X-ray diffraction (XRD) with Cu-K α target in 2θ ranges between 20° and 80°. TEM specimens were prepared by a conventional twin-jet polishing technique using an electrolyte mixture of HClO₄, C₄H₄OH and CH₃OH. TEM analysis was performed to investigate the morphologies of both TN9Z and TN9ZM using Philips CM20 operating at 200 kV. Tensile stress–strain tests were carried out at an initial strain rate of $1.67 \times 10^{-3} \text{ s}^{-1}$ using an Instron 5567 Materials Test System (MTS) at room temperature. Extensometer was applied to measure the strain.

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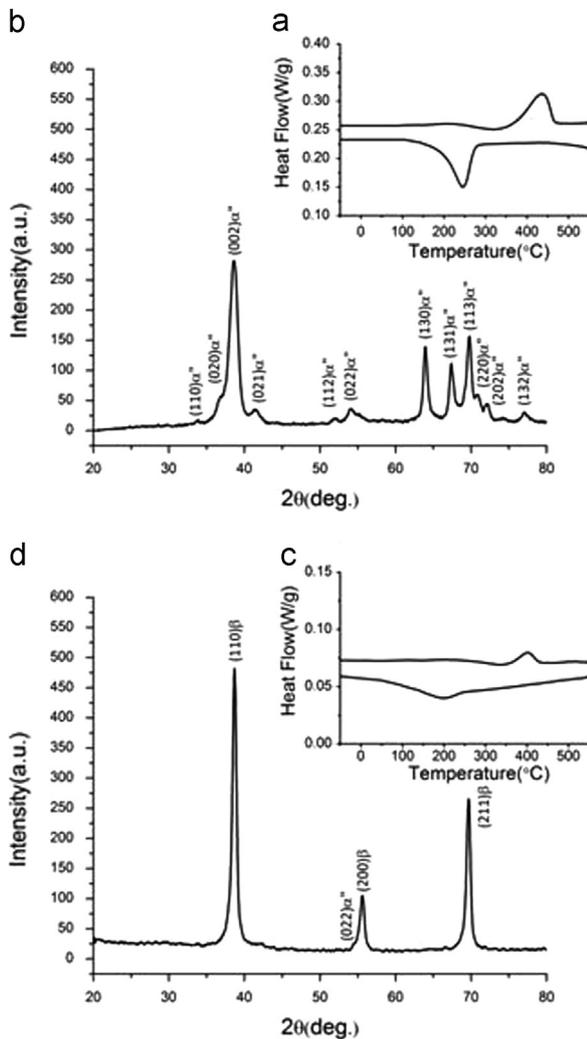


Fig. 1. DSC curves of (a) TN9Z and (c) TN9ZM, as well as the corresponding XRD profiles of (b) TN9Z and (d) TN9ZM.

3. Results and discussion

DSC measurement and XRD analysis are conducted to obtain the martensitic transformation temperatures and characterize the crystallographic structures, respectively of both alloys. Fig. 1 shows the DSC curves of (a) TN9Z and (c) TN9ZM, as well as the corresponding XRD profiles of (b) TN9Z and (d) TN9ZM.

A distinct pair of transformation peaks upon heating and cooling are obtained in TN9Z (Fig. 1a), indicating that TN9Z undergoes a thermoelastic one step β to α'' martensitic transformation upon cooling from 600 °C. It is consistent with the XRD result that shows a high volume fraction of orthorhombic α'' phase (Fig. 1b). It should be noted that this orthorhombic α'' phase relates to shape memory behavior in numerous studies of β titanium alloys [6]. By adding 1 at% of Mo to TN9Z, the thermoelastic one step martensitic transformation upon heating and cooling is still obtained (Fig. 1c). However, all transformation temperatures and energies are decreased. This is in agreement with the β stabilizing effect of Mo in Ti-based alloys [7]. The martensitic start (M_s), martensitic finish (M_f), austenitic start (A_s) and austenitic finish (A_f) temperatures and their transformation energies of martensite (E_M) as well as austenite (E_A) of both TN9Z and TN9ZM are summarized in Table 1.

Zhou et al. [8] reported that the addition of Co or Mn to TiNi alloy results in the formation of randomly distributed point

Table 1
Transformation temperatures and energies of both alloys.

	Transformation temperatures (°C)				E_M (J/g)	E_A (J/g)
	M_s	M_f	A_s	A_f		
TN9Z	267	148	359	485	13.1	22.0
TN9ZM	277	112	339	442	1.4	7.4

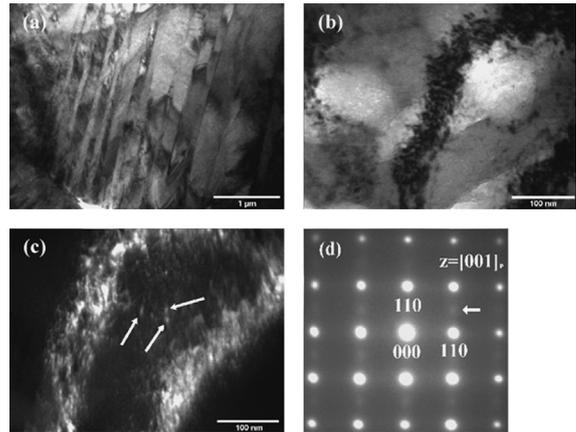


Fig. 2. Bright field TEM images of (a) TN9Z and (b) TN9ZM, as well as (c) the dark field TEM image and (d) corresponding SAD pattern at $[001]_\beta$ zone axis of TN9ZM.

defects, which generates random local stresses suppressing the formation of long range ordered martensites. On the other hand, Wang et al. [5] and Zhang et al. [9] also stated that further addition of Co or Mn leads the system transformation to the newly discovered strain glass state (a higher order transition) instead of the martensitic state (first order transition). Here, the decrease in transformation energies of TN9ZM should be related to the addition of Mo [10] which forms randomly distributed point defects causing the martensitic transformation becomes sluggish. Consistently, major body cubic β phase with a presence of small amount of peaks corresponding to α'' phase is detected in TN9ZM (Fig. 1d).

Fig. 2 shows the bright field TEM images of (a) TN9Z and (b) TN9ZM, as well as (c) the dark field TEM image and (d) corresponding SAD pattern at $[001]_\beta$ zone axis of TN9ZM.

A typical lamellar structure of self accommodated α'' martensite is observed in TN9Z (Fig. 2a). This is consistent with the XRD result (Fig. 1b). Instead, nanosize martensites are found to grow preferential at the grain boundaries in TN9ZM (Fig. 2b). Fig. 2c shows the corresponding dark field TEM image of TN9ZM shown in Fig. 2b. The preferential grow of martensites on grain boundaries have been previously studied in Ni rich TiNi alloys and are related to the multiple-step martensitic transformation [11]. It is suggested the reason for the preferential grow of martensites on grain boundaries in the present alloy is linked to the microstructural heterogeneity and localized coherency stress fields induced by the addition of Mo. Furthermore, nanodomains, marked by small white arrows, are clearly observed within the grain interior (Fig. 2c). Similar nanodomain structures were also reported in TiNi based SMA associating with the premartensitic phenomena and short range ordering of martensites [12]. Fig. 2d shows the corresponding SAD pattern of nanodomains at $[001]_\beta$ zone axis in TN9ZM. The pattern unveiled the β structure with superlattice spots at $\{h + (1/2)k + (1/2)0\}$ and diffused streaky along $\langle 110 \rangle_\beta$ directions. Tahara et al. [13] suggested that these diffuse streaks along $\langle 110 \rangle$ directions with maxima at $1/2$ positions

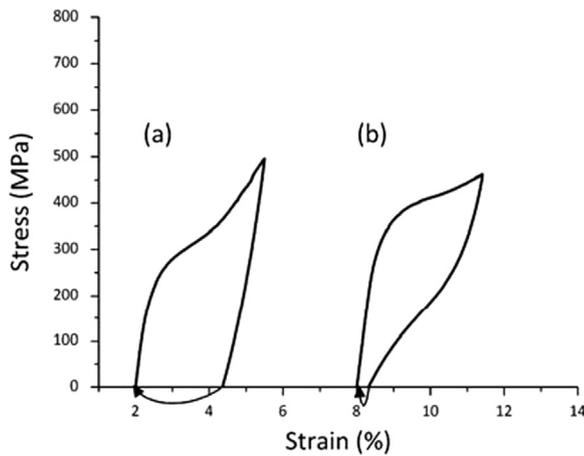


Fig. 3. SS curves of (a) TN9Z and (b) TN9ZM at room temperature.

were due to a $\{110\}_\beta < 1\bar{1}1 >_\beta$ type transverse lattice modulation in the β phase of Ti23Nb10 alloy. The lattice modulation of the β phase is resulted from the relaxation of the local strain field caused by the introduction of interstitial atoms to the bcc structure. Hence, it is suggested that the addition of Mo to the TN9Z would cause a similar effect on martensitic transformation with that by adding oxygen to the TiNb alloys [13].

Fig. 3 shows the stress–strain (SS) curves of (a) TN9Z and (b) TN9ZM at room temperature.

The SS curves show strikingly difference by adding 1 at% of Mo to TN9Z. In Fig. 3a, TN9Z shows a typical deformation behavior of SMA with a plateau of around 2% in strain. Upon heating after unloading, the strain induced after loading and unloading is fully recovered as indicated by an arrow below the SS curve. In contrast, a combination of $\sim 3.1\%$ superelastic strain and complete SME is obtained in TN9ZM after unloading from a 3.5% strain at room temperature (Fig. 3b) suggesting the TN9ZM is in unfrozen strain glass state (i.e. glass transition temperature $-T_0 < 25^\circ\text{C}$), although the A_f is above room temperature. It is believed that the mechanism of this superelasticity (exhibits below M_f), is different from that of other typical SMA [4]. Again, Tahara et al. [13] suggested that the origin of the superelasticity is related to the local barriers of nanodomains which suppress martensitic transformation in Ti–23Nb–10 alloy. For TN9ZM, the thermoelastic martensitic transformation is suppressed by randomly distributed point defects (nanodomains). However, the alloy still exhibits stress-induced martensitic transformation upon loading. Similar behavior has been reported in the $\text{Ti}_{48.5}\text{Ni}_{51.5}$ alloy [14] that the strain glass state can transform to favorable single variants under stress since its driving force has sufficiently overcome the kinetic limitation of the local barriers. Therefore, the mechanism of superelasticity in the present alloy is suggested to be attributed to the nanodomains which oppose to the stress-induced and growth of the favorable single variants from the strain glass state upon loading.

4. Conclusions

To summarize, our new strain glass alloy, Ti19Nb9Zr1Mo (at%), shows a great difference in microstructure and exhibits a combination of a good superelasticity of $\sim 3.1\%$ and complete SME at room temperature. The mechanism of this superelasticity is related to the randomly distributed point defect which opposes to the formation and growth of the favorable single variants.

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