Superelasticity and Tunable Thermal Expansion across a Wide Temperature Range

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Materials that undergo a reversible change of crystal structure through martensitic transformation (MT) possess unusual functionalities including shape memory, superelasticity and low/negative thermal expansion. These properties have many advanced applications, such as actuators, sensors and energy conversion, but are limited typically in a narrow temperature range of tens of Kelvin. Here we report that, by creating a nano-scale concentration modulation via phase separation, the MT can be rendered continuous by an in-situ elastic confinement mechanism. Through a model titanium alloy, we demonstrate that the elastically confined continuous MT has unprecedented properties,

such as superelasticity from below 4.2 K to 500 K, fully tunable and stable thermal expansion, from positive, through zero, to negative, from below 4.2 K to 573 K, and high strength-to-modulus ratio across a wide temperature range. The elastic tuning on the MT, together with a significant extension of the crystal stability limit, provides new opportunities to explore advanced materials.

Key words: Ti alloy, Superelasticity, Thermal expansion behavior, Temperature characteristic

1. Introduction

Martensitic transformation (MT) is a typical first-order diffusionless phase transformation^[1–7]. One of its unique characteristics is the displacive and cooperative atomic movement (shear + shuffle, with shear being the dominant mode) taking place within a narrow temperature (T) range, with a strong autocatalysis like an avalanche in a speed of sound propagation^[5,6]. This intrinsic character is crucial for the thermal-induced shape memory (SM) effect, making its operation both T -sensitive and reliable^[5–7]. Some applications^[8–11], such as in-depth space exploration require stable SM materials that function across a wide T -range of hundreds Kelvin. However, all current SM alloys (SMAs) exhibit the stress-induced superelasticity (SE) within only a narrow T -range (tens of Kelvin) and with a large hysteresis^[8,12]. Their T -range of low/negative thermal expansion (LTE/NTE) is about one tenth of that of ferromagnetic Invar alloys^[11].

In this study, we explore the possibility of changing the fundamental characteristics of an MT from a typical strong first-order (discontinuous) to “continuous”. This work was inspired by the recently-developed multifunctional titanium alloys with high strength and low elastic modulus^[13–15]. An example of such alloys is Ti–15Nb–2.5Zr–4Sn (at.%), abbreviated as Ti2448 from its weight percent composition Ti–24Nb–4Zr–8Sn, where β (bcc) $\rightarrow \alpha'$ (orthorhombic) MT takes place^[14–19]. The alloy exhibits continuous elastic softening with increasing stress from 0 MPa to at least 850 MPa (Fig. 1(a, b))^[15,16], which is in sharp contrast to the typical stress–strain curve of SMAs that exhibits a stress plateau due to the abrupt MT^[1]. This novel stress–strain behavior leads us hypothesize that Ti2448 has yet-to-be-detected microstructural heterogeneities that confines the MT. Such confinement is also responsible for the other unique feature of the MT, i.e., it is solely stress-induced rather than both thermal- and stress-induced (Fig. 1(c–e)), unexpected for normal thermoelastic MT^[1]. In view of the previous findings, a nano-scale concentration modulation is feasible to confine

the MT because the stress-induced martensite is localized abnormally in ~ 2.5 nm equiaxed regions^[17,18], unlike micron-scale internally twinned martensitic plates commonly observed in SMAs^[1].

Here we demonstrate that Ti2448 has indeed a unique nano-scale compositional architecture consisting of interpenetrating Nb-rich and Nb-lean domains. Since the Nb-rich domains are more stable (having much lower martensitic starting T , M_s), they elastically confine the MT in the neighboring Nb-lean domains. *This nano-scale elastic confinement fully suppresses the autocatalysis as well as the T -induced MT, and the transformation becomes continuous and solely stress-induced.* Accompanying such an elastically confined MT is SE over a wide T -range from below 4.2 K to 500 K, which is about 10 times of the SE T -range observed for the classic SMA, NiTi. As the MT is stress-induced, this alloy's thermal expansion is fully tunable up to 625 K and thermally stable up to 573 K, which is ~ 100 K higher than that of the classic ferromagnetic Invar alloy, FeNi. Together with its high strength-to-modulus ratio (4–5 times of other metallic materials, such as stainless steel) and good ductility across a wide T -range, the alloy has great potential for integrated functional and structural applications.

2. Experimental

An ingot of Ti2448 alloy with a diameter of 380 mm was fabricated by vacuum arc melting by using a Ti–Sn master alloy and pure Ti, Nb and Zr as raw materials. The ingot was hot-forged at 1123 K to form round bars of 55 mm in diameter and then hot-rolled at 1073 K to 12 mm in diameter.

The uniaxial cyclic loading and unloading tensile tests were conducted on an MTS-SANS CMT 5000 machine equipped with a CryoLab low temperature system and an Epsilon 3542 low temperature extensometer by using samples with a gauge section of 5 mm in diameter and 25 mm in length at an initial strain rate of $2.5 \times 10^{-4} \text{ s}^{-1}$. The tests were carried out at 4.2–398 K, which were controlled by a Keithley 2000 Multimeter system. The thermal expansions were measured by a Linseis L78/ RITA dilatometer in helium atmosphere at 293–573 K with a heating and cooling rate of 3 K/min.

The synchrotron X-ray diffraction (SXRD) analyses were performed on beamline ID-11-C at

advanced photon source (APS), Argonne National Laboratory (ANL) using 113 keV X-ray with a wavelength of 0.0112 nm and beam size of $250 \mu\text{m}^2$. A 1.5-mm thick band shaped sample was exposed with the longitudinal axis perpendicular to the X-ray beam. Diffraction patterns were collected by a 2D digital detector.

The atom probe tomography (APT) samples were cut into small rods with 0.5 mm in diameter and 20 mm in length, which were electro-polished in a solution containing HClO_4 (5%), 2-butoxyethanol (35%) and methanol at 233 K under a voltage of 50 V, and then sharpened with a Zeiss Auriga FIB until the tip radius was less than 100 nm. The prepared samples were field evaporated by using a Cameca LEAP 4000X SI instrument. The analyses were carried out in laser pulsing mode at 23 K with a target evaporation rate of 5 ions per 1000 pulses, a pulse rate of 250 kHz, a laser energy of 80 pJ and a laser spot size of $\sim 2 \mu\text{m}$. The wavelength of the UV laser was 355 nm. The APT data were reconstructed and analyzed using IVAS 3.6.6TM software.

3. Result and Discussion

To explore the hypothesized nano-scale heterogeneity in composition, 3D APT was performed by using a local electrode atom probe^[20]. Non-uniformity in composition was indeed observed, consisting of Nb-rich and Nb-lean domains that are 2–3 nm in size and are approximately equiaxed in shape. Three iso-concentration surfaces showing 3D Nb-rich domains are plotted in Fig. 2(a) for Nb contents of 18.5, 17.0 or 16.5 at.%. The volume fraction of the Nb-rich domains delineated by the iso-surface increases as the Nb content for creating the surface approaches the nominal Nb concentration of 15.1 at.%. 2D cross-sections of the 3D APT data in the form of Nb and Ti distribution maps (Fig. 2(b)) show the interpenetrating Nb(Ti)-lean and -rich domains, typical of continuous phase separation^[21,22]. The phase separation was confirmed to be iso-structural because only the single β phase was detected by SXRD measurements conducted at 400 K (Fig. 1(c)).

To illustrate the nano-scale Nb concentration modulation, a 1D schematic is provided in Fig. 2(c). This unique Nb modulation leads to a periodical variation in properties because the β phase with lower content of Nb is less stable against the $\beta \rightarrow \alpha''$ MT, resulting in lower elastic modulus (E), larger MT strain (ε_{MT}) and higher M_s ^[23–25], but has better recovery (larger ε_{MT}), as compared to the more stable Nb-rich domains, as shown in Fig. 2(c) for E and ε_{MT} . Thus, the Nb-rich domains form a

3D nano-scale elastic confinement architecture that regulates the MT of the Nb-lean domains.

The confinement is so strong that the thermally-induced MT is completely suppressed in the alloy. According to the well-known theory of cubic crystal^[26,27], the β phase stability is governed by the shear modulus c' ($= (c_{11} - c_{12})/2$, c_{ij} is elastic constant), which is positive for an elastic stable crystal and becomes negative otherwise (Born criterion). The Nb-lean domains with the lowest stability, corresponding to Nb content of ~8 at.% in Fig. 2(b), have $M_s \sim 600$ K^[23,24]. However, the SXRD profile at 100 K (Fig. 1(d)) reveal that the alloy is single β phase, except for weak diffusion scattering, implying that even undercooling as large as ~500 K is insufficient to trigger the MT. Thus, the Nb-lean β phase has positive c' far below its M_s , i.e., its stability limit is extended significantly by the nano-scale elastic confinement. Note that the Nb-rich domains with the highest Nb of ~20 at.% should exhibit high c' , corresponding to an extremely low $M_s \sim 0$ K^[23–25]. Thus the nano-scale 3D compositional architecture provides a way to extend significantly the crystal stability limit.

To evaluate the elastic confinement on the phase stability of the Nb-lean domains, the extended Born criterion^[26] is modified here to be $c' = c'_{\text{Nb-lean}} + c'_{\text{Nb-rich}}$, revealing that the MT of the Nb-lean domain is possible only when the elastic confinement of the Nb-rich domain can be overcome. Since both driving force for and the elastic resistance to the MT are stronger at lower T , the MT in the alloy has an extremely weak T dependence as compared with that in normal SMAs (Fig. 1(d)). Since both MT of the Nb-lean domains and elastic deformation of the Nb-rich domains are coupled together, the large scale elastic deformation of the latter leads to high strength over wide T range, overcoming the sharp T -dependent strength for the normal SMAs. It should be noted in the following analysis that the SE of Ti2448 is defined as the total recovery during loading release because the elastic strain of the Nb-rich domains and the MT strain of Nb-lean domains cannot be separated like the normal SMAs. For normal SMAs, the parent phase passes through a T -dependent region from the small scale linear elastic deformation stage to the suddenly triggered MT stage.

As expected, the alloy is functional and strong in a wide T range (Figs. 3, 4). Firstly, its SE is over a wide T -range. From the cyclic stress–strain curves and their recoverable strains varied with the applied strain and T , the data in Fig. 3(a) show clearly that the SE increases as T decreases to 150 K and then remains almost constant up to 4.5% as T further decreases to close to absolute zero (4.2 K). From extrapolation of the linear section of Fig. 3(a), the alloy would be expected to exhibit normal linear elasticity with a strain of less than 1% at ~500 K. Thus, the alloy is SE over ~500 K,

about one-order of magnitude larger than that of existing SMAs such as NiTi^[1].

The residual deformation after the SE can be recovered further as T is increased via SM. At 6% strain at 77 K, the alloy has ~4.25% SE (unloading at 77 K) and ~1.25% SM (heat to room T under unloading), i.e., the total recoverable strain is ~5.5% (Fig. 3(a)). This value is much larger than the SE+SM strain of β -Ti SMAs, which is generally below 3%^[23,24]. It is also unexpected for Ti2448 because the previous SXRD analysis showed that the stress-induced MT results in an average MT strain of ~2.25% at room T ^[18], i.e., the total recoverable strain (~5.5% at 77 K) is ~2.5 times of the MT strain at room temperature (Fig. 3(b)). This breaks the MT theory that the sum of the SE and SM cannot exceed the limit of the MT strain, as shown in Fig. 3(b) for Ni–Ti and Ti–Nb SMAs^[8,24]. The enhancement is caused by the Nb-lean domain with the merit of large MT strain, e.g., the Nb-lean domains with 8 at.% Nb have a MT strain as high as 9% (Fig. 2(c)). The new relationship in Fig. 3(b) suggests that both SE and its upper temperature limit can be further improved by decreasing Nb in the alloy.

Secondly, its σ/E ratio is high with good ductility over a wide T -range. The alloy has high σ/E ratio of ~2.0%, which is as high as that observed for brittle amorphous materials, and good ductility of ~20% at room temperature^[15]. The ratio is ~5 times of that of comparable alloys such as Al and Mg (Fig. 3(c)). Most importantly, the alloy exhibits two inverse strengthening relationships with other crystalline materials including SMAs and Gum Metal. As shown by the linear arrow in Fig. 3(c), the $\langle 100 \rangle$ single crystal has the highest σ/E ratio of ~2.5%, followed by the hot-rolled specimen with fine grains that has a lower ratio of ~2.0%, and the aged specimen with α phase precipitates, which has the lowest ratio of ~1.5%. This inverse order implies that the strengthening effect by the elastically confined MT is much greater than that from those well-known mechanisms such as grain refinement and precipitation. Furthermore, the current alloy exhibits an increased σ/E ratio from 1.35 to 3.05 as T decreased from 398 K to 20 K. This is in sharp contrast with high strength SMAs that soften quickly in a narrow T -range with decreasing temperature towards M_s ^[28]. Thus, the nano-scale elastically confined MT offers the advantages of SMAs having high strength and elastic solids being stronger at lower temperature.

Lastly, its tunable thermal expansion (TE) is across a wide T -range. As to the normal SMAs, in which the MT is the first-order with strong autocatalysis, the T -range of TE can be widen significantly by deformation^[29,30], e.g., a cold-worked Cu-based SMA has a thermal cycle stable

T -range of ~ 200 K and a upper limit of ~ 360 K^[29]. Both are lower than these of the ferromagnetic Invar alloys^[11]. Recent investigations have found that the cold-worked Gum Metal has a much larger T -range of TE of ~ 500 K, with a thermal stable limit up to ~ 473 K^[13,31,32]. Here we demonstrate that both can be extended by about 100 K for Ti2448 alloy. Since the SMA has a lower T limit of TE below its M_s ^[29], the SE at 4.2 K (Fig. 3(a)) supports that the lower limit of our alloy is less than 4.2 K. Thus, the exploration focuses on its upper limit, in particular of thermal cycle stable limit.

To produce the martensitic embryos, the alloy was deformed to 3%, 6% and 9% at room temperature and then thermally cycled between 293 and 573 K. At the 3% deformation, the alloy exhibits a normal linear thermal expansion with a coefficient thermal expansion (CTE) of 9×10^{-6} K⁻¹ (Fig. 4(a)), which remains constant for the following cycles (Fig. 4(b)). For the 6% and 9% deformation, the reversible embryos lead to a thermal contraction of $\sim 0.2\%$ and $\sim 0.9\%$ in turn during the first heating (Fig. 4(a)), which were mistaken as NTE in some publications. Here it reveals that the first heating after the deformation is just a training step to obtain the novel thermal expansion behavior: the second heating cycle leads to the linear LTE/NTE, with CTEs of about 1×10^{-6} K⁻¹ and -7×10^{-6} K⁻¹ (Fig. 4(b)). After such a training, they are thermal stable over 30 heating and cooling cycles up to 573 K (Fig. 4(c)). Furthermore, the CTE and the applied strain follow a linear relation (Fig. 4(d)), which is significant because the CTE is fully adjustable by controlling the amount of deformation from positive to negative through zero. Additionally, its upper limit T is ~ 625 K, ~ 50 K higher than its thermal stable limit.

4. Conclusion

We have shown through a model titanium alloy that the fundamental characteristics of MT are tunable by nano-scale elastic confinement via 3D concentration modulation generated by continuous phase separation. The elastically confined MT offers unprecedented functional properties of SE and tunable thermal expansion across a wide T -range and an excellent combination of mechanical properties such as being flexible (low E), strong (high σ/E ratio) and ductile at the same time. This new discovery opens a new avenue for the design of new SMAs and improvement of existing SMAs with confined MT via nano-scale chemical composition modulations.

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Figure Caption

Fig. 1. Stress-induced continuous elastic softening of Ti2448 alloy by a novel MT: (a) cyclic stress-strain curves with a total strain of 6% at an interval of 1% (measured at 293 K); (b) an enlarged curve in a with the cycle strain up to 1% showing that the softening starts at the beginning of the loading; (c, d) 2D synchrotron X-ray diffraction (SXRD) profiles measured at 400 K and 100 K, showing the single β phase without the thermal-induced MT; (e) 2D SXRD profile of the unloaded alloy after 9% deformation (both measured at 300 K), showing the stress-induced MT to the α'' martensite.

Fig. 2. Nano-scale Nb modulation and its induced periodical properties: (a) three examples of 3D Nb-rich iso-concentration surfaces, where Nb is 18.5, 17.0 or 16.5 at.% (left to right); (b) a pair of 2D cross-sections showing Nb and Ti distributions; (c) schematics of 1D periodical Nb modulation, and the corresponding periodical variations of both elastic modulus (E) of the β phase and its MT strain (ε_{MT}) to form the α'' martensite.

Fig. 3. The combined SE and high strength in wide temperature range: (a) both SE and SM strains vary with T ; (b) new relation of the recovered strain with the MT strain (the data of Ti2448 alloy measured at 77 K); (c) high σ/E ratio and its inverse strengthening relation with other metallic materials noted by the linear arrow.

Fig. 4. Tunable thermal expansion in a wide temperature range up to 573 K: (a) unstable thermal expansion for the first heating cycle, a step to control the followed heating cycle stability; (b) thermal expansion being normal, zero (LTE) and negative (NTE) for the second cycle. Note that the contraction is $\sim 0.2\%$, which is much lower than the value of $\sim 0.9\%$ for the first heating; (c) thermal stable NTE for 25–32 heating cycles; (d) tuning the coefficient of thermal expansion (CTE) via pre-deformation.

Figure List

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