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Low-alloy content Ti-Mo-based alloys with large superelasticity and narrow stress hysteresis for potential biomedical applications

Shuanglei Li^a, Xu Wang^a, Tae-Hyun Nam^b, Junha Yang^c and Jong-Taek Yeom^c

^aCollege of Materials Science and Engineering, Huaqiao University, Xiamen, People's Republic of China; ^bDepartment of Materials Engineering and Convergence Technology & Research Institute for Green Energy Convergence Technology (RIGET), Gyeongsang National University, Jinju, Republic of Korea; ^cTitanium Alloys Department, Metal Materials Division, Korea Institute of Materials Science (KIMS), Changwon, Republic of Korea

ABSTRACT

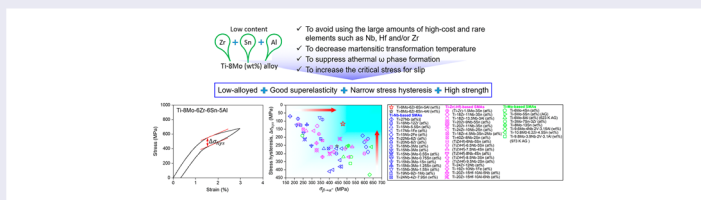
In most Ni-free Ti-Nb- and Ti-Zr-based superelastic alloys, large amounts of high-cost and rare elements such as Nb, Ta, Hf and/or Zr are contained, increasing the cost and fabrication difficulty of the alloy. Here, new low-alloy content Ti-Mo-Zr-Sn-Al alloys are developed with large room temperature superelasticity and narrow stress hysteresis for potential biomedical applications. A good combined performance of yield stress (477 MPa) and small stress hysteresis (117 MPa) is achieved at room temperature in Ti-8Mo-6Zr-6Sn-5Al (wt%) alloy showing a recovery strain of 4.4%, which has not been obtained in previously reported Ni-free Ti-Nb, Ti-Zr and Ti-Mo-based superelastic alloy.

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KEYWORDS

Ti-Mo-Zr-Sn-Al alloy; shape memory alloys; superelasticity; stress hysteresis; athermal ω phase



1. Introduction

The superelasticity of shape memory alloys (SMAs) is of great interest for biomedical devices such as superelastic orthodontic wires, endodontic files in dentistry and superelastic bone staples in orthopedics [1–3]. In most Ni-free Ti-Nb-based and Ti-Zr-based SMAs showing room temperature superelasticity for these biomedical applications, high amounts of Nb and/or Zr (Nb, Zr or Nb + Zr > 30 wt%) accompanied by some minor β -stabilizing elements such as Mo, Ta, Fe and/or Sn are contained [4]. The high amounts of Nb and/or Zr inevitably increase the cost and fabrication difficulty of SMAs. Ti-Mo alloys with low Mo content such as Ti-10Mo (wt%) are reported to show superelasticity at room temperature [5] and are expected to be cost-effective and practical SMAs for developing economical implants. However, similar to most Ti-Nb-based SMAs, the main drawback of Ti-Mo-based SMAs is the small recovery strain that

is not compared with that in the Ti-Zr-based SMAs and thus it is necessary to improve the superelasticity of Ti-Mo-based SMAs.

Superelasticity in Ti-Nb, Ti-Zr and Ti-Mo-based SMAs is attributed to the reversible stress-induced martensitic transformation between β parent phase (body-centered cubic) and α'' martensite phase (orthorhombic structure) [1]. The lattice deformation strain generated by the formation of α'' martensite from β parent phase, particularly, along the principal axes of $[010]_{\alpha''}$ (i.e. η_2), is known to be an important factor in determining the superelastic recovery strain [1]. In binary Ti-Mo alloys, η_2 decreases with increasing Mo content [6] and thus Ti-Mo alloys with low Mo content have a high ability to obtain a large lattice deformation strain. It is reported that Ti-8Mo (wt%) alloy exhibits a large η_2 ($\sim 8.5\%$) [4,6] and is thought to be a promising candidate to obtain high superelastic recovery strain. However, the

CONTACT Shuanglei Li ✉ li.sixstones@hqu.edu.cn College of Materials Science and Engineering, Huaqiao University, Room B511, Pan-Chinese Science Hall, Xiamen 361021, People's Republic of China; Jong-Taek Yeom ✉ yjt96@kims.re.kr Titanium Alloys Department, Metal Materials Division, Korea Institute of Materials Science (KIMS), Changwon 51508, Republic of Korea

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M_s ($\beta \rightarrow \alpha''$ martensitic transformation start temperature) of this alloy is as high as 515°C [6], making it impossible to obtain the superelasticity at room temperature. Thus, a large amount of β -stabilizing elements are needed to add in Ti-Mo alloys to decrease M_s and then further to obtain room temperature superelasticity.

To avoid using the high-cost and rare elements such as Nb, Hf and Ta, low-cost Sn and Al are the better choice to add to Ti-Mo alloys. Additionally, Sn is a highly biocompatible element and Al is regarded as an acceptable element for implantation [7]. It is well known that the additions of Sn and Al not only largely decrease M_s of Ti-(Nb, Zr or Mo)-based SMAs but also effectively suppress the formation of athermal ω (ω_{ath}) phase [2,4,8–10]. As thus, a narrow stress hysteresis is expected to obtain in superelastic alloys as a result of suppressing ω_{ath} phase formation, which is additionally preferable for SMAs to take advantage of a high recovery force [2]. The narrow stress hysteresis in SMAs, that is, the minimal difference between the stress required to induce martensite transformation and that required to recover its original shape by reverse transformation, is particularly beneficial in biomedical devices because it leads to reduced energy dissipation during cyclic loading and unloading and thus provides more precise control over the deformation and recovery of SMAs as well as improves fatigue resistance. Thus, the narrow stress hysteresis makes SMAs well-suited for various implants, surgical tools, and other medical devices that require accurate and repeatable actuation. The addition of Zr and Al to Ti-Nb and/or Ti-Zr-based SMAs is reported to increase η_2 effectively by tailoring the lattice parameters of α'' and β [11,12]. Therefore, the low content of Zr, Sn and Al added to Ti-8Mo (wt%) alloy is expected to obtain superelasticity with large recovery strain at room temperature by simultaneously decreasing the M_s and keeping high η_2 and also to show a narrow stress hysteresis by suppressing the ω_{ath} phase formation.

In this study, new low-alloy content Ti-8Mo-6Zr-6Sn-(0–5)Al (wt%) alloys are designed without using high contents of Nb, Ta, Hf and/or Zr to develop superelastic alloys with narrow stress hysteresis for biomedical applications. With increasing the Al content from 3 to 5 wt%, superelastic behavior becomes more clear. The maximum recovery strains in 4Al and 5Al specimens are measured to be 4.3% and 4.4%, respectively. The stress hysteresis in 3Al, 4Al and 5Al specimens are measured to be 330, 256 and 117 MPa, respectively and the yield stress in these three specimens is 319, 443 and 477 MPa, respectively. It is found that a good combination performance of a yield stress of 477 MPa and a narrow stress hysteresis of 117 MPa is achieved in the Ti-8Mo-6Zr-6Sn-5Al

Table 1. Nominal and actual chemical compositions of the studied Ti-8Mo-6Zr-6Sn-(0–5)Al (wt%) alloys.

Alloy	Nominal composition (wt%)	Actual composition (wt%)					
		Mo	Zr	Sn	Al	O	Ti
0Al	Ti-8Mo-6Zr-6Sn	6.91	5.35	5.57	–	0.065	Bal.
1Al	Ti-8Mo-6Zr-6Sn-1Al	6.95	5.46	5.56	1.09	0.066	Bal.
2Al	Ti-8Mo-6Zr-6Sn-2Al	7.37	5.88	5.96	2.27	0.069	Bal.
3Al	Ti-8Mo-6Zr-6Sn-3Al	7.28	5.68	5.79	3.24	0.068	Bal.
4Al	Ti-8Mo-6Zr-6Sn-4Al	7.54	5.92	5.91	3.93	0.070	Bal.
5Al	Ti-8Mo-6Zr-6Sn-5Al	7.76	5.88	6.16	4.59	0.078	Bal.

alloy which also exhibits room temperature superelasticity with a recovery strain of 4.4%.

2. Materials and method

Ti-8Mo-6Zr-6Sn-(0–5)Al (wt%) (TMZSA) ingots were fabricated by arc melting and then sealed in a quartz tube with a vacuum and homogenized at 1000°C for 2 hrs followed by ice-water quenching. Each homogenized ingot was cold-rolled at room temperature to a sheet with a thickness of about 0.55 mm (thickness reduction ratio: about 94%). The actual chemical compositions of the TMZSA alloys were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 720EX) and the oxygen content in the alloy was measured by oxygen/nitrogen/hydrogen elemental analyzer (ONH836, LECO). The nominal and actual chemical compositions of the produced TMZSA alloys are shown in Table 1.

The cold-rolled sheets were solution-treated at 900°C for 30 min with a vacuum followed by ice-water quenching. X-ray diffraction (XRD) measurement was done with Cu K α radiation at room temperature. The martensitic transformation temperatures of the solution-treated TMZSA specimens were evaluated by differential scanning calorimetry (DSC, TA instrument Q20) at a heating and cooling rate of 10 °C/min. In the DSC measurements, all the TMZSA specimens were initially cooled to –80 °C and held for 3 min, then their DSC curves corresponding to the subsequent heating and cooling processes were recorded. Tensile tests (strain rate: $1.67 \times 10^{-4} \text{ s}^{-1}$) were done at room temperature by using specimens with a dimension of 2.5 mm (width) $\times$ 0.5 mm (thickness) $\times$ 50 mm (length). The gage length was 30 mm and the tensile direction was set parallel to the specimen's rolling direction. The microstructure was investigated by a transmission electron microscope (TEM, Model: JEM 2100F) operated at 200 kV by using specimens prepared by the conventional twin-jet polishing at about 233 K using a solution of 93% methanol, 5% H₂SO₄ and 2% HF (in volume).

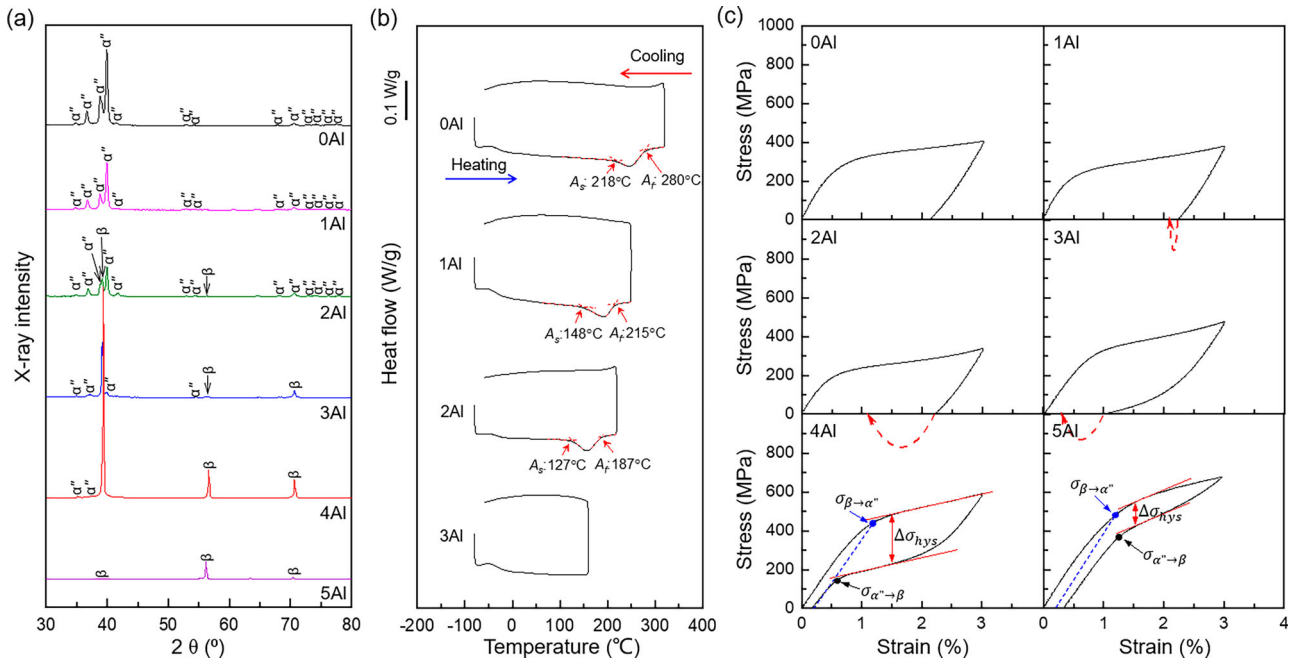


Figure 1. XRD patterns (a), DSC curves (b) and loading-unloading stress-strain curves (c) of the TMZSA specimens solid-solution treated at 900°C for 30 min. The red dashed lines with arrows below the stress-strain curves in (c) represent the recovery strain due to the shape memory effect.

3. Results and discussion

Figure 1(a) shows XRD patterns obtained at room temperature of TMZSA alloys. As Al content increases from 0 to 5 wt%, phase constitution evolves from full α'' marten-site to a single β phase. The XRD patterns indicate that the increase in Al content in TMZSA alloys decreases the M_s and the 5Al specimen's M_s is below room temperature. Thus, Al is thought to work as a β-stabilizing element in present TMZSA alloys, as reported in Ti-Zr and Ti-Nb-based SMAs [13,14]. To detailly measure the transformation temperatures of TMZSA alloys, DSC measurements were done. As shown in Figure 1(b), only one endothermic peak corresponding to α'' → β reverse transformation in the DSC heating curves of 0Al, 1Al and 2Al specimens is observed and any DSC peaks during the heating and cooling processes are not observed in the 3Al, 4Al and 5Al alloy specimens (DSC curves of 4Al and 5Al alloy specimens are not shown here). The A_s (α'' → β reverse martensitic transformation start temperature) and A_f (α'' → β reverse martensitic transformation finish temperature) decrease from 218 to 127°C, from 280 to 187°C, respectively, with increasing Al content from 0 to 2 wt%. The DSC measurements further verify that the Al additions decrease the transformation temperatures of TMZSA alloys. The loading-unloading stress-strain curves of TMZSA alloys obtained at room temperature are shown in Figure 1(c). After unloading, the specimens

were heated to 200°C to investigate the shape memory effect. Neither superelasticity nor shape memory effect is observed in 0Al specimen. Only a very small recovery strain of 0.1% due to the shape memory effect is observed in 1Al specimen. The shape memory recovery strain increases to 1.1% in 2Al specimen. Both superelasticity and shape memory effect are observed in 3Al specimen and only superelasticity is observed in 4Al and 5Al specimens.

The critical stress for inducing β → α'' martensitic transformation (σ_{β→α''}) in 4Al and 5Al specimens is measured by the 0.2% offset method. The σ_{β→α''} (indicated by a blue single-headed arrow) in 4Al and 5Al specimens is measured to be 443 and 477 MPa, respectively. σ_{α''→β} represents the stress at which the α'' marten-site → β reverse transformation finishes. The stress hysteresis (Δσ_{hys}) in superelastic stress-strain curves is defined by the difference in plateau stress during loading (β → α'' martensite) and unloading (α'' marten-site → β) at 1.5% of the applied strain of 3% [15] or the difference between σ_{β→α''} and σ_{α''→β} at the case of unobvious plateau stress as shown in Figure 1(c). The Δσ_{hys} of 4Al and 5Al specimens are measured to be 256 and 117 MPa, respectively. A comparison map of Δσ_{hys} vs σ_{β→α''} of typical Ni-free Ti-Nb-, Ti-Zr(-Hf)- and Ti-Mo-based SMAs [2–4,11,14,16–39] is shown in Figure 2(a). The detailed specimen information of these cited SMAs is summarized in Table S1 (Supplementary

materials). The $\Delta\sigma_{hys}$ is taken from the superelastic loading-unloading stress-strain curves obtained at/or near room temperature with the applied strain of 2.5–3%. For superelastic Ti-Nb, Ti-Zr and Ti-Mo-based SMAs, the $\sigma_{\beta \rightarrow \alpha''}$ is taken as yield stress. Clearly, the 5Al alloy is towards the wanted area of a high yield stress and narrow stress hysteresis as indicated by the red arrows as shown in Figure 2(a). Figure 2(b) shows a comparison map of $\Delta\sigma_{hys}$ vs alloying element contents in typical Ni-free Ti-Nb, Ti-Zr and Ti-Mo-based SMAs. Compared with certain Ti-Nb and Ti-Zr-based SMAs that show relatively smaller $\Delta\sigma_{hys}$ such as Ti-18Zr-13.5Nb-3Al (at%) (120 MPa) and Ti-18Zr-11Nb-3Sn (at%) (130 MPa), 5Al specimen with $\Delta\sigma_{hys}$ of 117 MPa consists of much lower contents of alloying elements and avoids the addition of large amounts of high-cost and rare-metal elements of Nb and/Zr (Nb, Zr or Nb + Zr > 30 wt%). Also, compared with Ti-Mo-based SMAs generally consisting of low alloying contents (15–20 wt%), the 5Al specimen exhibits much smaller $\Delta\sigma_{hys}$. Thus, a good combination of narrow stress hysteresis and low alloying element contents is achieved in the 5Al specimen.

Since the superelasticity with narrow stress hysteresis is more applicable than the shape memory effect in biomedical devices such as guide wires, orthodontic wires and stents in blood vessels, the superelastic behaviors of 4Al and 5Al specimens were investigated in detail by cyclic tensile tests. The cyclic stress-strain curves of 4Al and 5Al specimens obtained at room temperature are shown in Figure 3(a and b), respectively. Both alloys show clear room temperature superelasticity. The recovery strain (ε_r) as a function of applied strain is shown in Figure 3(c). The ε_r vs applied strain curves of other superelastic Ti-Mo-based SMAs in literature are also shown in Figure 3(c) for comparison. The maximum ε_r (ε_r^{max}) in 4Al and 5Al specimens is found to be 4.3% and 4.4%, respectively, which is higher than those of other typical Ti-Mo-based SMAs such as Ti-Mo [5], Ti-Mo-Sn [4,16–18], Ti-10.8Mo-6.2Zr-4.5Sn (wt%) (Beta III) [38] and Ti-9.8Mo-3.9Nb-2V-3.1Al (wt%) [39] alloys.

For metallic biomaterials such as orthopedic implants, high yield strength is required since the sudden fracture of load-bearing implants can be avoided due to the high yield strength and thus ensure the implants work for a long period [40]. Also, a narrow stress hysteresis is very beneficial for achieving a high recovery force since the energy loss is small during the loading and unloading cycle [2]. For ensuring the biomechanical compatibility of implants, the SMAs are recommended because their unique superelastic behavior with large recovery strains can mimic the natural biomechanical properties of bone [41]. Unfortunately, the combination properties

Table 2. Comparison of $\sigma_{\beta \rightarrow \alpha''}$, $\Delta\sigma_{hys}$ and ε_r^{max} measured by cyclic loading-unloading tensile tests of Ti-8Mo-6Zr-6Sn-(4, 5)Al and typical superelastic Ni-free Ti-Nb, Ti-Zr and Ti-Mo-based shape memory alloys subjected to solid-solution treatment or aging treatment for biomedical applications.

Alloy	$\sigma_{\beta \rightarrow \alpha''}$ (MPa)	$\Delta\sigma_{hys}$ (MPa)	ε_r^{max} (%)	Ref.
Ti-8Mo-6Zr-6Sn-5Al (wt%)	477	117	4.4	This study
Ti-8Mo-6Zr-6Sn-4Al (wt%)	443	256	4.3	This study
Ti-15Nb-3Mo-1.25Sn (at%)	271	121	3.7	[2]
Ti-15Nb-3Mo-1.5Sn (at%)	344	78	2.1	[2]
Ti-3Mo-7Sn-3Zr (at%)	245	190	5.1	[3]
Ti-8Mo-13Sn (wt%)	509	252	3.1	[4]
Ti-18Zr-13.5Nb-3Al (at%)	220	120	6.1	[14]
Ti-5Mo-5Sn (at%)	500	260	3.5	[16,17]
Ti-6Mo-4Sn (at%)	525	320	4.0	[18]
Ti-18Zr-11Nb-3Sn (at%)	330	130	6.0	[19]
Ti-24Zr-10Nb-2Sn (at%)	310	160	7.0	[21]
Ti-18Zr-4.5Nb-3Sn-2Mo (at%)	250	150	6.2	[22]
(Ti-Zr)–1.5Mo-3Sn (at%)	340	180	7.0	[25]
Ti-40Zr-8Nb-2Sn (at%)	360	220	5.5	[26]
Ti-9.8Mo-3.9Nb-2V-3.1Al (wt%)	520	360	3.4	[39]

of high yield strength, narrow stress hysteresis and large recovery strain have not been obtained in the previously reported Ni-free Ti-Nb, Ti-Zr and Ti-Mo-based SMAs until now.

The magnitudes of $\sigma_{\beta \rightarrow \alpha''}$, $\Delta\sigma_{hys}$ and ε_r^{max} of the present TMZSA alloys and other typical Ti-Nb, Ti-Zr and Ti-Mo-based SMA [2–4,14,16,18,21,22,25,26] are listed in Table 2. It is seen that a good combined performance of $\sigma_{\beta \rightarrow \alpha''}$ (477 MPa), small $\Delta\sigma$ (117 MPa) and large recovery strain (4.4%) is achieved in 5Al specimen. Such good room temperature superelasticity with narrow stress hysteresis of 5Al alloy specimen is reported for the very first time in Ti-Mo-based SMAs. For a typical Ni-free Ti-Zr-based SMA, Ti-18Zr-11Nb-3Sn (at%), it exhibits the largest ε_r^{max} (6.0%) among the reported Ni-free Ti-based SMAs as well as a narrow stress hysteresis of about 130 MPa at the first cycle of the stress-strain curve [19]. However, the $\sigma_{\beta \rightarrow \alpha''}$ of Ti-18Zr-11Nb-3Sn (at%) alloy is about 330 MPa which is lower than that (477 MPa) in the 5Al specimen with a narrower stress hysteresis of 117 MPa. Among Ni-free Ti-Nb-based SMAs, the smallest stress hysteresis of 78 MPa was reported in a Ti-15Nb-3Mo-1.5Sn (at%) SMA while its ε_r^{max} is only 2.1% [2]. The ε_r^{max} of 3.7% with a stress hysteresis of 121 MPa was obtained in Ti-15Nb-3Mo-1.25Sn (at%) SMA while its $\sigma_{\beta \rightarrow \alpha''}$ is only 271 MPa [2] which is much smaller than that (477 MPa) in 5Al specimen. Simultaneously possessing large room temperature superelasticity, narrow stress hysteresis and high yield stress are achieved in the low-alloy content Ti-Mo-Zr-Sn-Al alloys by varying Al content.

To investigate the reasons for the decrease in $\Delta\sigma_{hys}$ in the present study, the microstructures of 4Al and 5Al specimens were observed by TEM. Figure 4 shows the

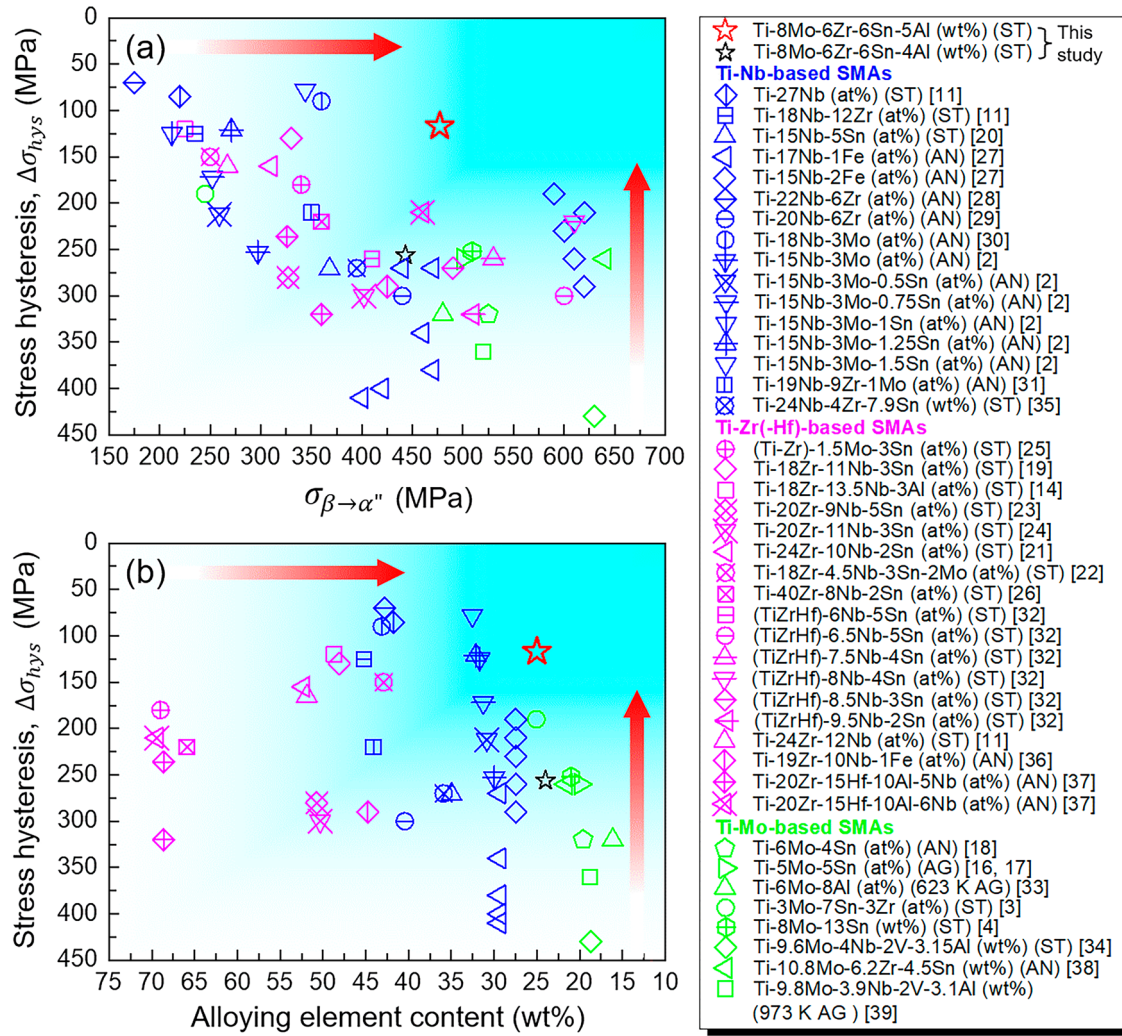


Figure 2. Comparison maps of stress hysteresis ($\Delta\sigma_{hys}$) vs $\sigma_{\beta \rightarrow \alpha''}$ (a) and stress hysteresis ($\Delta\sigma_{hys}$) vs alloying element content (b) of 4Al and 5Al alloy specimens in the present study and other typical superelastic Ni-free Ti-Nb-, Ti-Zr(-Hf)- and Ti-Mo-based shape memory alloys subjected to solid-solution treatment (ST), annealing (AN) or aging treatment (AG) [2–4,11,14,16–39]. The $\sigma_{\beta \rightarrow \alpha''}$ represents the critical stress for inducing $\beta \rightarrow \alpha''$ martensitic transformation. Alloy compositions in at% in alloys are converted to wt% in (b) for comparison. The red arrows in (a) represent the desired properties of narrow stress hysteresis and high yield strength ($\sigma_{\beta \rightarrow \alpha''}$) and those in (b) represent the desired alloys with low content of alloying elements and narrow stress hysteresis.

selected area diffraction patterns (SADPs) taken from the zone axis of $[1\bar{1}3]_{\beta}$ and the corresponding dark-field (DF) images obtained by using circled diffraction spots. Clear ω spots in SADP are observed in the 4Al alloy specimen as shown in Figure 4(a) whereas the intensities of the ω reflections become very faint in the 5Al specimen, which suggests that the amount of the ω_{ath} phase decreases remarkably. The DF images taken from the ω diffraction spot in each SADP clearly show the reduction in the amount of ω_{ath} phase as shown in Figure 4(a1 and b1). Thus, it is concluded that the increase in Al content suppresses the ω_{ath} phase formation in β matrix. Since the contents of Mo, Zr, Sn and oxygen keep similar

levels in 4Al and 5Al alloys as shown in Table 1, the superelastic property change (Figure 3) and microstructural evolution (Figure 4) are assuredly related to the Al content.

When only think about the effect of Al content on the $\sigma_{\beta \rightarrow \alpha''}$ (i.e. the absence of ω_{ath} in β matrix), the increase in Al content will lower martensitic transformation temperatures (MTTs), which is substantiated by the XRD patterns and DSC curves as shown in Figure 1, consequently leading to the increases in the gap between M_s and the test temperature (i.e. room temperature). As a result, $\sigma_{\beta \rightarrow \alpha''}$ of β matrix without ω_{ath} monotonically increase with increasing Al content as shown

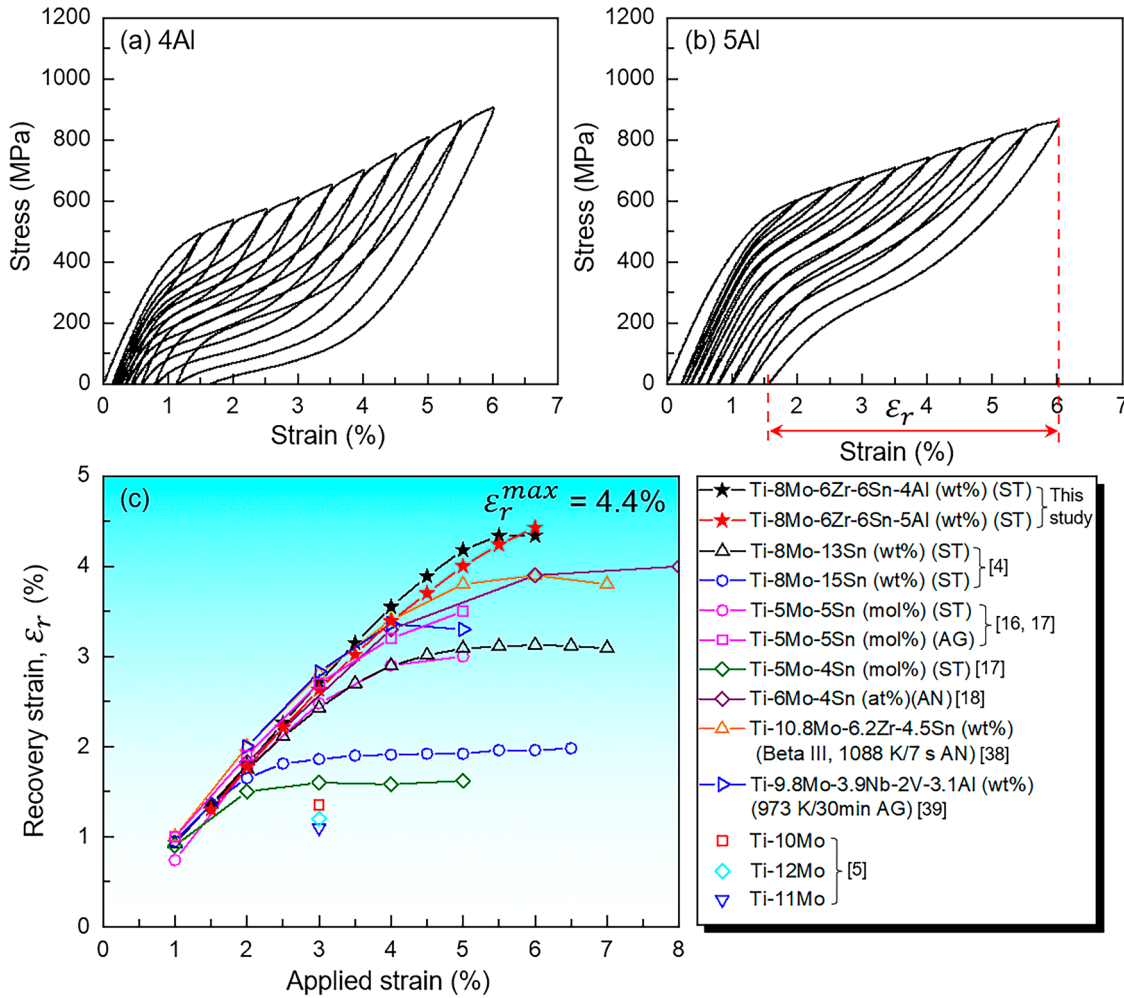


Figure 3. Cyclic loading-unloading stress-strain curves obtained at room temperature of the 4Al (a) and 5Al (b) alloy specimens solid-solution treated at 900°C for 30 min. The applied strain of the first cycle is set as 1.5% and is increased by 0.5% in each following cycle. (c) The plot of recovery strain (ε_r) as a function of the applied strain of 4Al and 5Al alloy specimens in the present study and other typical superelastic Ni-free Ti-Mo-based shape memory alloys subjected to solid-solution treatment (ST), annealing (AN) or aging treatment (AG) [4,5,16–18,38,39].

in Figure 5(a). However, it is known that ω_{ath} phase in β matrix suppresses the martensitic transformation (MT) and thus the stress for inducing martensite (i.e. $\sigma_{\beta+\omega_{ath}\rightarrow\alpha''}$) increases with increasing the amount of ω_{ath} [2,3]. In this regard, the $\sigma_{\beta\rightarrow\alpha''}$ of 4Al specimen ought to be higher than that in 5Al specimen because 4Al specimen contains higher ω_{ath} amount than the 5Al specimen as shown in Figure 4. The present result of the higher $\sigma_{\beta\rightarrow\alpha''}$ in 5Al specimen suggests that the role of Al content in the $\sigma_{\beta\rightarrow\alpha''}$ is dual, liking the role of Sn in $\sigma_{\beta\rightarrow\alpha''}$ reported in Ti-Nb-Mo-Sn alloys [2].

A schematic explanation of the dual role of Al content in the $\sigma_{\beta\rightarrow\alpha''}$ in this study is shown in Figure 5(b), which is adapted from Refs. [2,9]. The increase in Al content on the one hand suppresses ω_{ath} phase formation (leading to a decreased effect in $\sigma_{\beta\rightarrow\alpha''}$ as shown by the green

line), while on the other hand, it decreases MTTs (leading to an increased effect in $\sigma_{\beta\rightarrow\alpha''}$ as shown by the black line). Which role works dominantly depends on the Al content level. As a result, such a co-effect of Al on $\sigma_{\beta\rightarrow\alpha''}$ caused by the suppression of ω_{ath} and also the decrease in MTTs makes the $\sigma_{\beta\rightarrow\alpha''}$ as a function of Al content is not a single monotonical relationship, but exhibits a downward tendency at low Al content and an upward tendency at high Al content as represented by the red line. Such a behavior of Al content dependence of $\sigma_{\beta\rightarrow\alpha''}$ is similar to that of Sn on the $\sigma_{\beta\rightarrow\alpha''}$ in Ti-Nb-Mo-Sn alloys [2] and has been reported in the Ti-Mo-Al alloy system [9]. Thus, the 5Al specimen has a higher $\sigma_{\beta\rightarrow\alpha''}$ than 4Al specimen as a consequence of the dominant role of decreasing in MTTs accompanying with ω_{ath} phase suppression from 4Al to 5Al specimen.

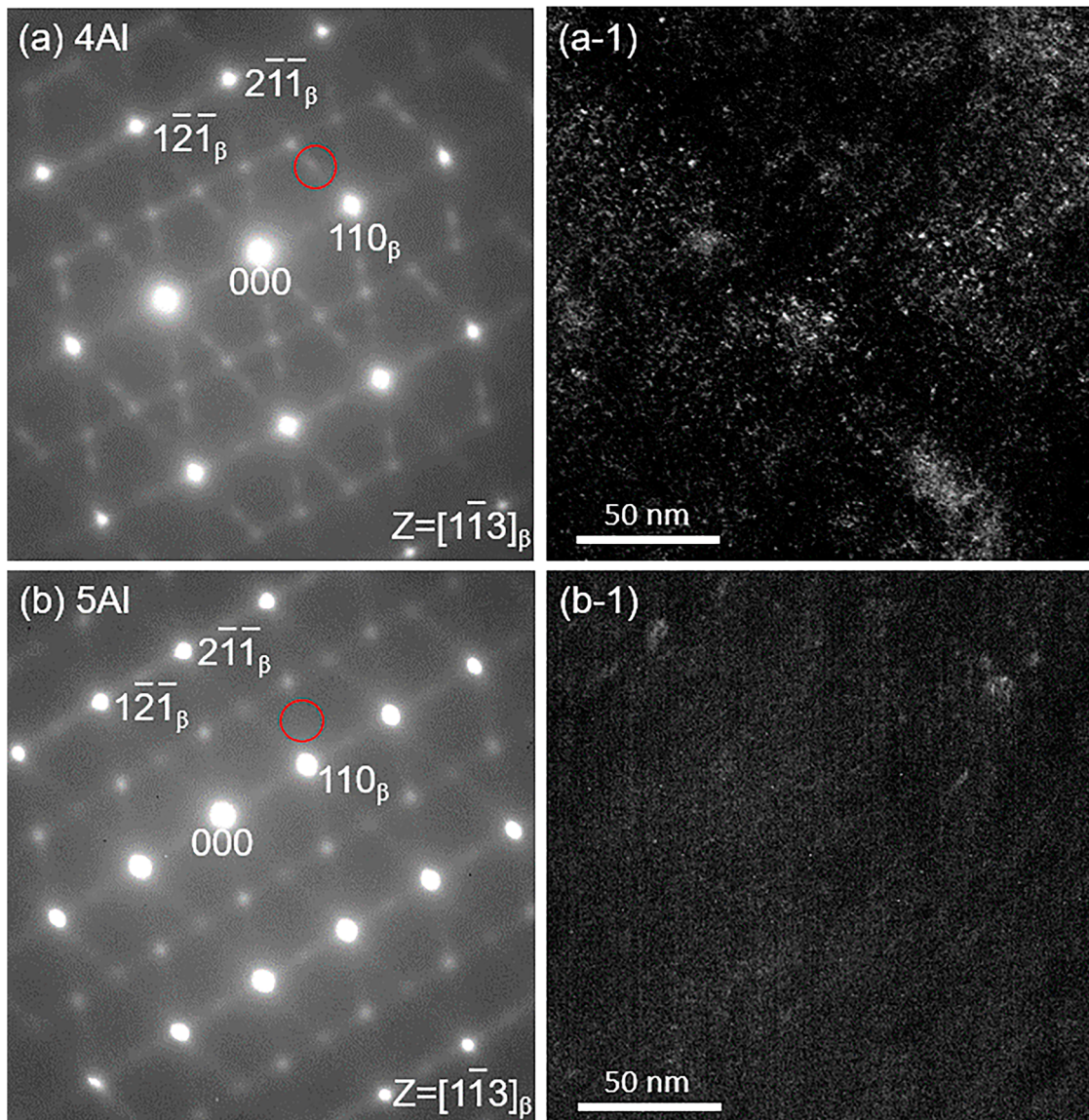


Figure 4. Selected-area diffraction patterns and the corresponding dark-field TEM images taken by the circled diffraction spots for the 4Al (a, a-1) and 5Al (b, b-1) alloy specimens solid-solution treated at 900°C for 30 min.

It has been reported that the ω_{ath} phase in β matrix also transforms into the α'' martensite along with the $\beta \rightarrow \alpha''$ transformation during loading, thus, there is no ω_{ath} phase in the stress-induced α'' phases [2,3,9,41, 42]. As a result, the $\sigma_{\alpha'' \rightarrow \beta}$ monotonically increase with increasing Al content as shown by the blue line whether the ω_{ath} phase exists in β matrix or not as shown in Figure 5(a and b). Therefore, a smaller $\Delta\sigma_{hys}$ is obtained in 5Al specimen as shown in Figure 5(b). Also, the increase in Al content enhances the solid-solution hardening effect, which increases the critical stress for the slip of β matrix. Stress hysteresis is related to the irreversible friction energy of the interface between austenite and martensite during phase transformation during loading and unloading [15,43]. The small $\Delta\sigma_{hys}$ in the 5Al specimen also

may be ascribed to the high critical stress for slip due to solid-solution hardening of the addition of high Al content since the high critical stress for slip suppresses the energy dissipation upon the forward/reverse martensitic phase transformation. As a result, it is thought that the small $\Delta\sigma_{hys}$ (117 MPa) in the 5Al specimen is most likely due to the suppression of ω_{ath} phase and the enhanced critical stress for slip.

4. Conclusion

In summary, new low-alloy content Ti-Mo-Zr-Sn-Al alloys with varying Al content are designed to develop practical Ni-free Ti-based SMAs for biomedical applications. It is found that Al works as a β -stabilizing element

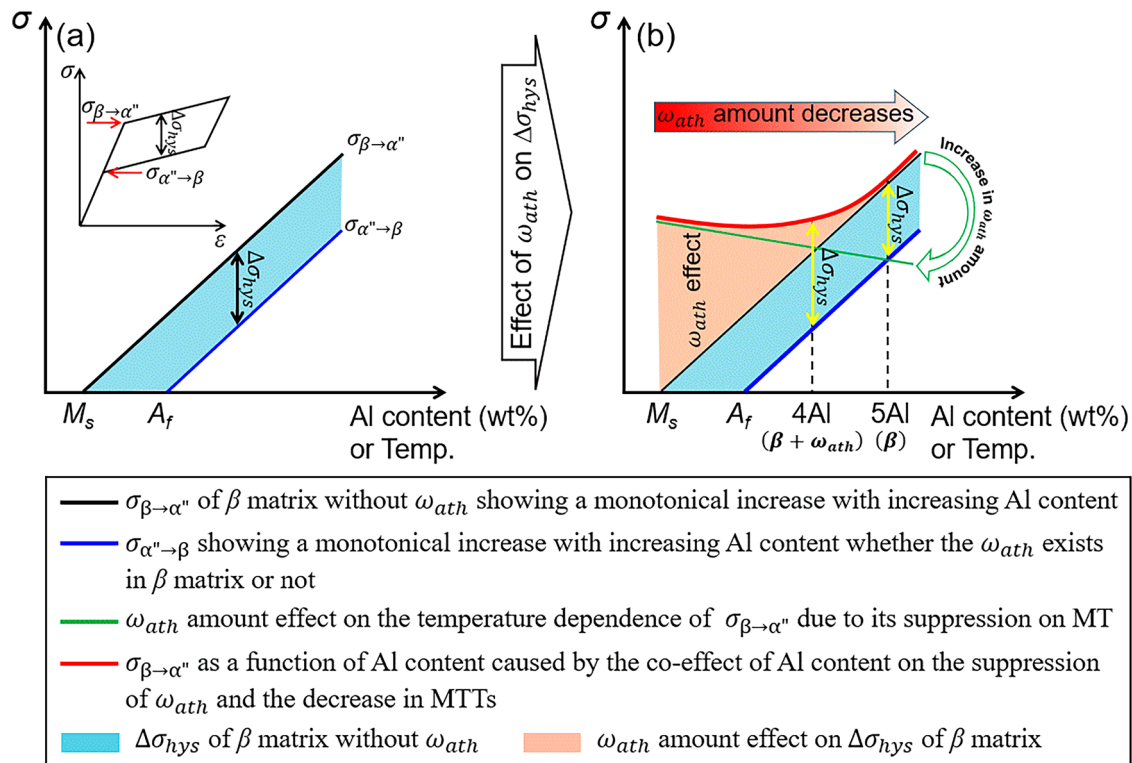


Figure 5. A schematic diagram showing the Al content dependence of $\sigma_{\beta \rightarrow \alpha''}$: (a) β matrix without ω_{ath} , (b) β matrix with ω_{ath} adapted from Refs. [2,9].

in the Ti-Mo-Zr-Sn-Al alloys and a good room temperature superelasticity is achieved in the Ti-8Mo-6Zr-6Sn-(4, 5)Al (wt%) alloys. The Ti-8Mo-6Zr-6Sn-5Al (wt%) exhibits a good combination performance of yield stress (477 MPa), narrow stress hysteresis (117 MPa) and large recovery strain (4.4%) at room temperature. The suppression of the athermal ω phase and the enhanced critical stress for slip are thought to be the reasons for the narrow stress hysteresis.

Disclosure statement

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