Development of high temperature Ti-Ta shape memory alloys

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Abstract. Recent development of Ti-Ta and Ti-Ta-Al high temperature shape memory alloys was reviewed. The effect of Ta content on shape memory behavior of Ti-Ta alloys was first described. Shape memory effect was confirmed in Ti-(30-40)Ta alloys. The Ms temperature decreased by 30K per 1at.% Ta. The amount of ω phase formed during aging decreased with increasing Ta so that stable high temperature shape memory effect was confirmed for Ti-32Ta (Ms=440K) during thermal cycling between 173K and 513K. Secondly, the effect of ternary alloying elements (X = V, Cr, Fe, Zr, Hf, Mo, Sn, Al) on the shape memory behavior of Ti-30Ta-X alloys was described. Among the alloying elements, Sn and Al were effective to suppress the effect of aging on the shape memory behavior, since they strongly suppress the formation of ω phase induced due to aging during thermal cycling. For this reason the Ti-30Ta-1Al and Ti-30Ta-1Sn alloys exhibited stable high temperature shape memory effect during thermal cycling. It is suggested that Ti-Ta based alloys are attractive candidates for the development of novel high temperature shape memory alloys.

1. Introduction

Shape memory alloys exhibit the shape memory effect and superelasticity, thus they are attractive for applications as advanced actuators and superelastic materials. Such unique properties originate from the crystallographically reversible martensitic transformation between a parent phase and a martensite phase. The martensitic transformation temperatures are important since they define the limitation temperature of their applications.

Shape memory alloys (SMAs) exhibiting martensitic transformation temperatures above 373 K are attractive for applications as advanced actuator and superelastic materials that can function in a hot environment, such as in home appliances (gas stove, heaters and many general appliances), transportation (automobile and aircrafts) and power generation systems (oil and gas energy plants). However, the martensitic transformation start temperature (Ms) of commercially available Ti-Ni-base alloys is below 373 K [1] so their applications are currently limited below 373 K. For this reason the development of high temperature shape memory alloys (HTSMAs) have been extensively pursued [2], such as Ti-Ni-X (X = Zr, Hf, Pd, Pt, Au), Ni-Al and Ni-Mn base HTSMAs. However the inherent poor cold workability of the existing HTSMAs makes them difficult to be fabricated into fine wires and thin plates with dimensions suitable for actual applications.

Recently the β-type Ti base shape memory alloys which exhibit excellent cold workability have been extensively investigated. For example the shape memory behavior of β-type Ti-base alloys, such as Ti-Mo [3-7], Ti-Nb [8-12] and Ti-Ta [13-16] alloys, has been reported. The excellent cold-workability of β-type Ti-base shape memory alloys have made them attractive for practical applications as new smart materials, since they can be easily fabricated to fine wires and thin plates of dimensions suitable for actual applications. However they are very sensitive to aging above 373 K, where ω phase forms during aging. If the ω phase forms and grows it can decrease the Ms temperature or completely suppress the shape memory effect. The application temperature for β-type Ti-base shape memory alloys is therefore limited to below 373 K. In an effort to increase the application temperature of β-type Ti-base shape memory alloys to temperatures above 373 K, it is important to suppress the formation of the ω phase.

In literature, several reports pointed out that ω phase can be suppressed by the addition of ternary

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alloying elements [17-19]. In this paper, high temperature Ti-Ta shape memory alloys are digested based on the recent results of the present authors [16, 20]. The following topics were described: 1) The transformation temperature, thermal stability and shape memory effect of Ti-Ta binary alloys, 2) The effect of different ternary alloying elements, including V, Cr, Fe, Zr, Mo, Hf, Al and Sn, on the shape memory behavior of Ti-Ta; 3) The effect of aging on the shape memory behavior in order to assess which elements are the most suitable to suppress the formation of ω phase in Ti-Ta base shape memory alloys; 4) Lastly the stability of high temperature shape memory effect during thermal cycling of selected ternary alloys.

2. About Ti-Ta alloys

The origin of shape memory behavior of β-type Ti base alloys is the reversible martensitic transformation between β parent phase and α" martensite phase. In order for these alloys to exhibit the shape memory effect it is necessary to obtain the β phase by the addition of β phase stabilizers such as Mo, Nb and Ta to Ti. Several reports have shown that β-type Ti-base shape memory alloys can exhibit martensitic transformation temperatures above 373K [14, 15, 21, 22]. However, the β-type alloys are sensitive to aging at intermediate temperatures (373~673K) where the thermal ω phase is formed [23-25]. The nucleation and growth of ω phase when exposed to temperatures above 373K can suppress the martensitic transformation and cause embrittlement. Therefore, an important issue for Ti-base shape memory alloys to be considered as HTSMA is the stability of their high temperature shape memory effect (Ms >373K).

Among the β-stabilizer elements (Mo or Nb or Ta), the substitution of Ta for Nb in Ti-Nb alloy was effective to suppress the formation of ω phase [9]. However there is no systematic investigation regarding the shape memory behavior and the amount of ω phase formed during aging in Ti-Ta binary shape memory alloys.

3. Transformation temperatures of Ti-Ta alloys

The Ms temperature for the Ti-Ta alloys was estimated from strain-temperature curves under a 50 MPa stress. The dependence of the transformation temperatures with respect to Ta content is shown in Fig. 1, where Ms and Af temperatures decreased by approximately 30K per 1 at.% Ta. Compared with other β-stabilizer elements such as Nb and Mo, Ta is considered a weak β-stabilizer. When the composition of the alloy was 40Ta, Ms temperature is below room temperature. On the other hand, alloys containing less than 40Ta have Ms temperatures above room temperature. Furthermore, the specimens containing less than 35Ta have Ms temperatures above 373K, so they can be considered as high temperature shape memory alloys.
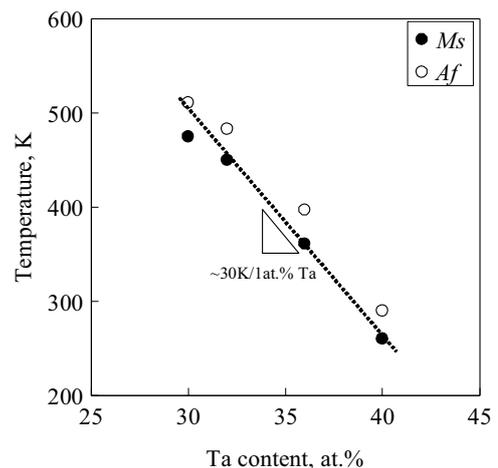

Fig. 1. Ms and Af temperatures of Ti-Ta solution-treated alloys.

4. Thermal stability of shape memory effect

To evaluate the thermal stability of shape memory effect, thermal cycling tests under a constant stress of 50MPa were carried out. Fig. 2 shows strain-temperature curves for Ti-32Ta solution-treated specimens which was (a) thermally cycled between 173K and 513K, and (b) thermally cycled between 173K and 573K. Another test was carried out to confirm the effect of holding (aging) the specimen at a high temperature (573K). As shown in Fig. 2(c) the first cycle was carried out by thermal cycling between 173K and 573K, and before performing the second cycle the specimen was held at 573K for 3.6ks. The shape memory effect was confirmed during thermal cycling between 173K and 513K as shown in Fig. 2(a). At the first cycle, Ms and Af temperatures were obtained to be 440K and 490K, respectively, and they decreased slightly with increasing number of cycles. However by increasing the thermal cycling range to between 173K and 573K, a notable decrease of transformation temperatures was observed. As shown in Fig. 2(b), the Ms temperature during the first cycle was about 440K and it decreased to 380K after five thermal cycles. Similarly decrease in transformation temperatures was observed after holding the specimen at 573K for 3.6ks as shown in Fig. 2(c). The Ms temperature during the first cycle was about 440K. Then the specimen was held at 573K for 3.6ks after the first thermal cycle. During the second thermal cycle the Ms temperature was measured as about 380K. The decrease in the transformation temperatures

during the thermal cycling suggests that the specimen underwent phase decomposition. It was confirmed by TEM observation that ω phase existed in a Ti-32at%Ta (Ti-32Ta) aged specimen.

In order to compare the thermal stability of Ti-Ta alloys with Ti-Nb alloys, a Ti-22Nb solution treated specimen was prepared. Based on previous reports [21] it is expected that the Ti-22Nb specimen will exhibit *Ms* temperature above 373K. Fig. 3(a) shows strain-temperature curves of the Ti-22Nb solution treated specimen obtained by thermal cycling between 173K and 513K under a constant stress of 50MPa. The shape memory effect above 373K was confirmed during the first thermal cycle with *Ms* temperature of 420K and *Af* temperature of 475K. The transformation temperature for Ti-22Nb is close to the transformation temperature of Ti-32Ta. After the first thermal cycle the strain-temperature curve of Ti-22Nb did not reveal shape memory effect during the second thermal cycle under the same thermal cycle condition, so the shape memory effect is considered unstable against thermal cycling. A similar experiment was performed using another specimen of the same composition, but this time the thermal cycle range was increased to between 173K and 573K, and the result is shown in Fig. 3(b). Increasing the maximum temperature to 573K in the thermal cycle range completely suppressed the shape memory effect of the specimen even during the first thermal cycle.

For the Ti-22Nb aged at 573K for 3.6ks, XRD measurement detected ω phase. It is suggested that the ω phase precipitated in the β phase during aging and it suppressed the martensitic transformation from the β phase to the α" phase after aging.
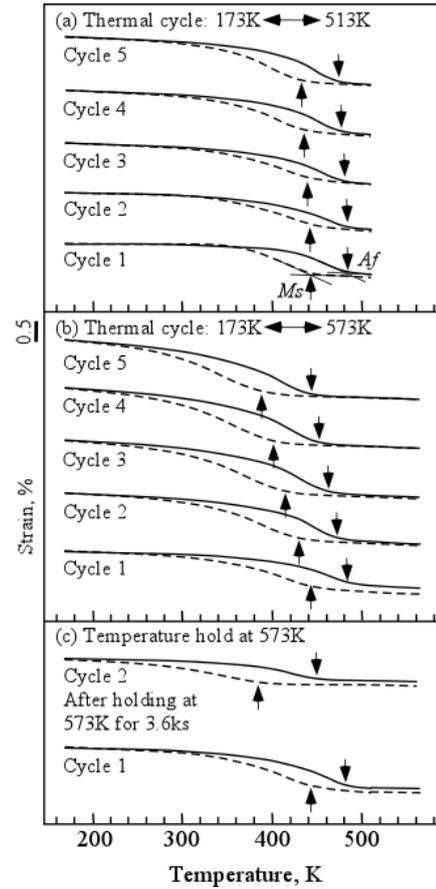

Fig. 2. Thermal cycle tests under a constant stress.

5. Relationship between ω phase formed by aging and *Ms* temperature

Fig. 4 shows a composition dependence of *Ms* temperature for Ti-Ta and Ti-Nb solution treated specimens. The *Ms* temperature of Ti-Ta decreased by 30K per 1at.%Ta as shown in Fig. 1 and the *Ms* temperature of Ti-Nb decreased by about 40K per 1 at.%Nb [10]. The *Ms* temperature for Ti-22Nb in this study was also plotted and it falls along the *Ms* line of Ti-Nb. As mentioned above the amount of ω phase decreases with increasing amount of β-stabilizing element, irrespective of the type of element, so it is indicated in Fig. 4 by an arrow. The dependence of the amount of ω phase formed during aging on the amount of β-stabilizer and the *Ms* temperature line for both alloy systems have important implications. For alloys having similar *Ms* temperature the composition of Ti-Ta is always rich with the β-sta-bilizing element compared with Ti-Nb, therefore the amount of ω phase that will form due to aging is expected to be less in Ti-Ta when compared with Ti-Nb. A similar
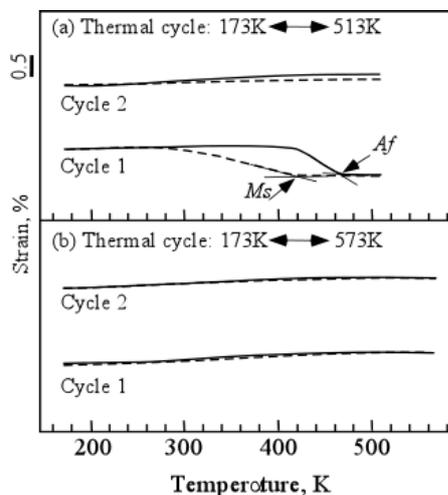

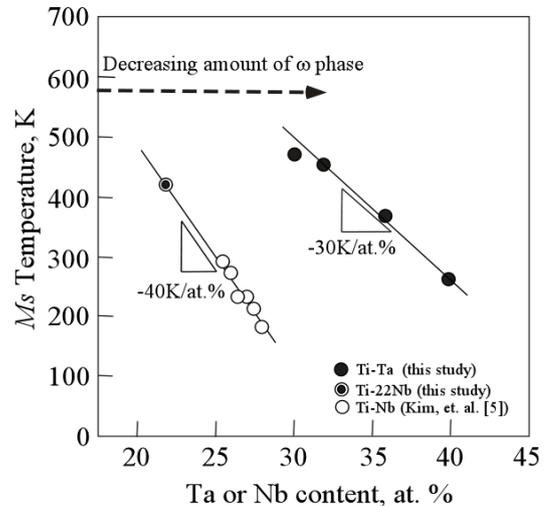**Fig. 3.** Thermal cycle tests under a constant stress in Ti-22Nb.

Fig. 4. *Ms* in Ti-Nb and Ti-Ta alloys.

argument can be surmise with Ti-Mo, since the addition of Mo can effectively decrease the *Ms* temperature [26] when compared with Nb and Ta. Hence for Ti-Mo alloys the ω phase is expected to form more easily and stable shape memory effect above 373K is very unlikely or difficult to confirm. These promising results imply that Ti-Ta is the most suitable base alloy system for the development of novel β-type Ti-base high temperature shape memory alloys. However it should be noted that further investigation is necessary to completely suppress the formation of ω phase during aging in Ti-Ta. Several suggestions include the investigation of the effect of ternary alloying elements and thermo-mechanical treatment on the stability of high temperature shape memory behavior in Ti-Ta base alloys.

6. β phase stability and shape memory behavior

Ti-Ta-X alloys were prepared by the Ar-arc melting method from high purity (99.9%) elemental sources. The Ta content was fixed at 30 at.% for all the alloys, and the amount of X (= V, Cr, Fe, Zr, Hf, Mo, Sn, Al) element added was varied up to 3 at.%. Hereafter the binary alloy is termed as 30Ta and the ternary alloys were termed according to the amount of element and its type, for example Ti-30at.%Ta-1at.%Al was denoted as 1Al alloy.

Fig. 5 shows a series of XRD profiles taken at room temperature for Ti-30Ta-1X solution treated specimens. The β phase (BCC structure) and α" phase (Orthorhombic structure) were observed, where the former is the parent phase and the latter is the martensite phase. It is also noted that the intense β(211) peak was due to texture development after solution treatment at 1173K of the cold-rolled specimen (98% thickness reduction). This type of texture was also reported for a Ti-22Nb-6Ta alloy [27], where the recrystallization texture of cold-worked specimen was $\{211\}\langle\bar{1}\bar{1}0\rangle$ of the β phase. The Ti-Nb base alloys are considered closely similar to Ti-Ta because of the similarity of their crystal structures and their tendency to undergo martensitic transformation, so the deformation mechanism and recrystallization behavior are expected to be closely similar. The β phase was observed for the 1Fe specimen and a mixture of β phase and α" phase was observed for the 1Cr specimen. For the other specimens only the α" phase were observed. These results suggest that Fe and Cr are strong β stabilizers against α" martensite phase when compared with the other alloying elements.

In order to determine the effect of the alloying element on the martensitic transformation temperatures, the *Ms* temperature was measured by tensile testing under various constant stresses during thermal cycling. The *Ms* temperature obtained at a 50 MPa stress during thermal cycling was considered as the *Ms* temperature of the alloy. For the sake of brevity only the strain-temperature curves at 50 MPa for Ti-30Ta-1X solution treated specimens are shown in Fig. 6. Shape memory effect was confirmed for all the specimens as manifested by the change in strain during thermal cycling; strain elongation due to the martensitic transformation on cooling (dashed line) and strain recovery due to the reverse transformation on heating (solid line). The *Ms* temperature decreased compared to the binary Ti-30Ta alloy, indicating that the β phase became more stable against α" martensite with the addition of the alloying element.
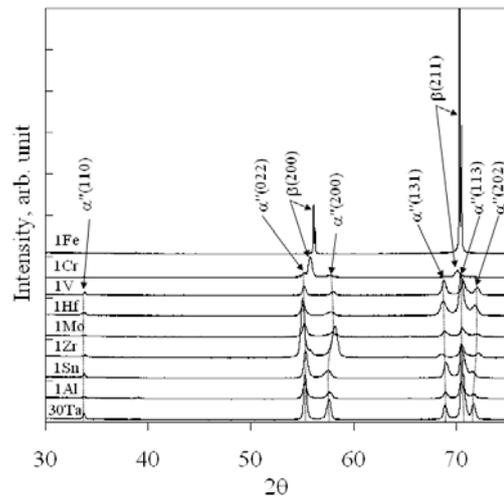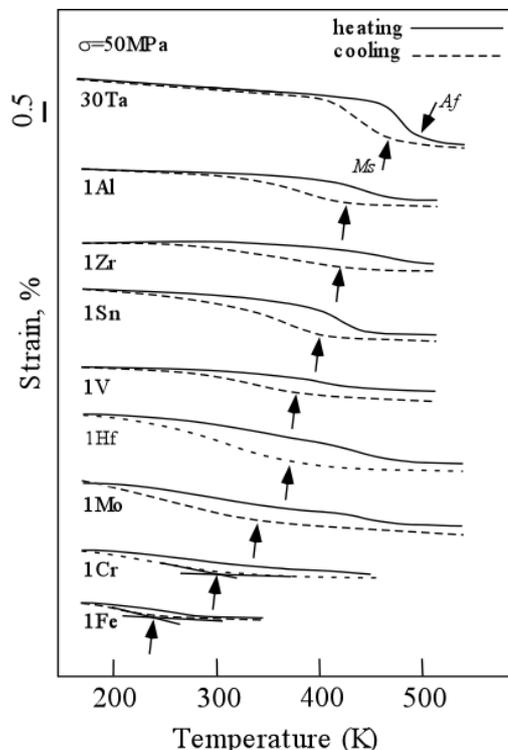

Fig. 5. XRD profiles of Ti-30Ta-1X alloys.

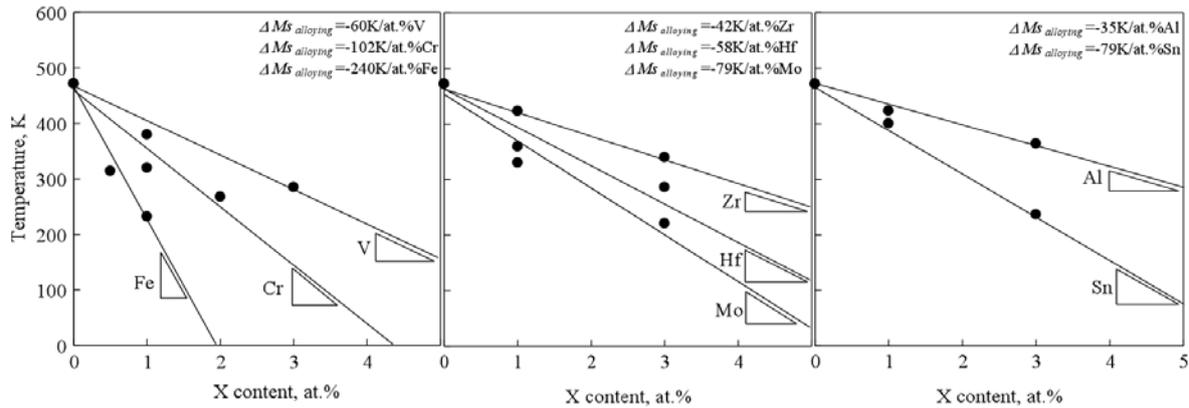**Fig.6.** Strain-temperature curves of Ti-30Ta-1X alloys.

Fig. 7. Ms as a function of alloying content for Ti-30Ta-X alloys.

Among these alloys only the 1Fe specimen has the Ms temperature below room temperature thus explaining the single β phase in the XRD profile (Fig. 5) for this specimen. The 1Cr specimen has Ms temperature near room temperature thus β phase was observed together with the α" phase in the XRD profile taken at room temperature. Whereas the other specimens have Ms temperatures well above room temperature, thus only the α" phase was observed. Composition dependence of the Ms temperature was clearly observed in Fig. 6, so in order to determine the composition dependence of Ms temperature in Ti-30Ta-X alloys quantitatively, the Ms temperature was plotted as a function of X content in Fig. 7. The Ms temperature decreases linearly for all the specimens, and the slope indicates the effectiveness of the alloying element to stabilize the β phase.

7. Effect of aging on the shape memory behavior

In order to investigate the effect of aging on the shape memory behavior of Ti-30Ta-X alloys, the solution treated specimens were aged at 573 K for 3.6 ks. Fig. 8 shows a plot of Ms temperature for the solution treated specimens and the aged specimens. For all the specimens the Ms temperature decreased after aging and the amount of decrease of Ms temperature due to aging is indicated as ΔMs_{aging}. The value of ΔMs_{aging} for 30Ta was more than 100 K. For the alloys containing the following elements, V, Cr, Fe, Zr, Hf and Mo, the value of ΔMs_{aging} was almost the same when compared with 30Ta, so it can be said that they are not effective to suppress the decrease of Ms temperature due to aging. On the other hand, the addition of Al and Sn decreased the value of ΔMs_{aging} to 66 K and 54 K, respectively, so it can be said that the additions of these elements were effective to suppress the effect of aging on the shape memory behavior.
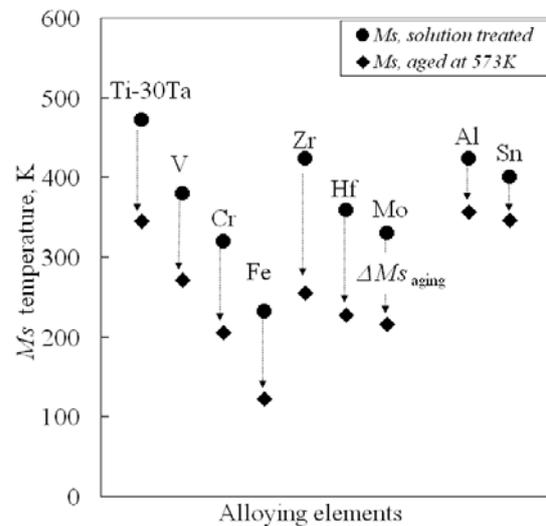

Fig. 8. Ms of Ti-30Ta-X alloys.

8. Thermal stability of shape memory effect in ternary alloys

In order to confirm the stability of high temperature shape memory effect, thermal cycling under a constant stress was performed on each of selected ternary alloys investigated in this paper. Among the ternary alloys 1V, 1Zr, 1Sn and 1Al have Ms temperature above 373 K (Fig. 6) in the solution treated condition, so they were selected for the thermal cycling tests. Fig. 9 shows the strain-temperature curves at 50 MPa stress of (a) 1V, (b) 1Zr, (c) 1Sn and (d) 1Al solution treated specimens thermally cycled between 173 K and 513 K up to 10 thermal cycles. For all specimens the shape memory effect was confirmed from the first cycle to the tenth cycle.

However the transformation temperatures (indicated by arrows pointing up and down as *Ms* and *Af*, respectively) were obviously affected by thermal cycling. For 1V (Fig. 9(a)) and 1Zr (Fig. 9(b)) specimens it is obvious that the transformation temperatures decreased with increasing thermal cycles. The *Ms* temperature reached lower than 373 K for both alloys after 10 thermal cycles. For 1Sn (Fig. 9(c)) and 1Al (Fig. 9(d)) the transformation temperatures were significantly stable during thermal cycling. The *Ms* temperature was maintained above 373 K for both alloys after ten thermal cycles. The *Ms* for each specimen was different so the decrease of *Ms* during thermal cycling was quantified by subtracting the *Ms* observed for each cycle from the *Ms* at the first cycle and the value was termed ΔMs_{cycle}. Fig. 10 shows the plot of ΔMs_{cycle} versus the number of cycles. The amount of decrease of *Ms* for 1V and 1Zr specimens was very drastic for the first five cycles and afterwhich the decrease of *Ms* became less, almost reaching a saturation level. On the other hand for 1Sn and 1Al specimens the amount of decrease of *Ms* was significantly smaller and they reached a saturation level without an initial drastic decrease. The total amount of decrease after 10 thermal cy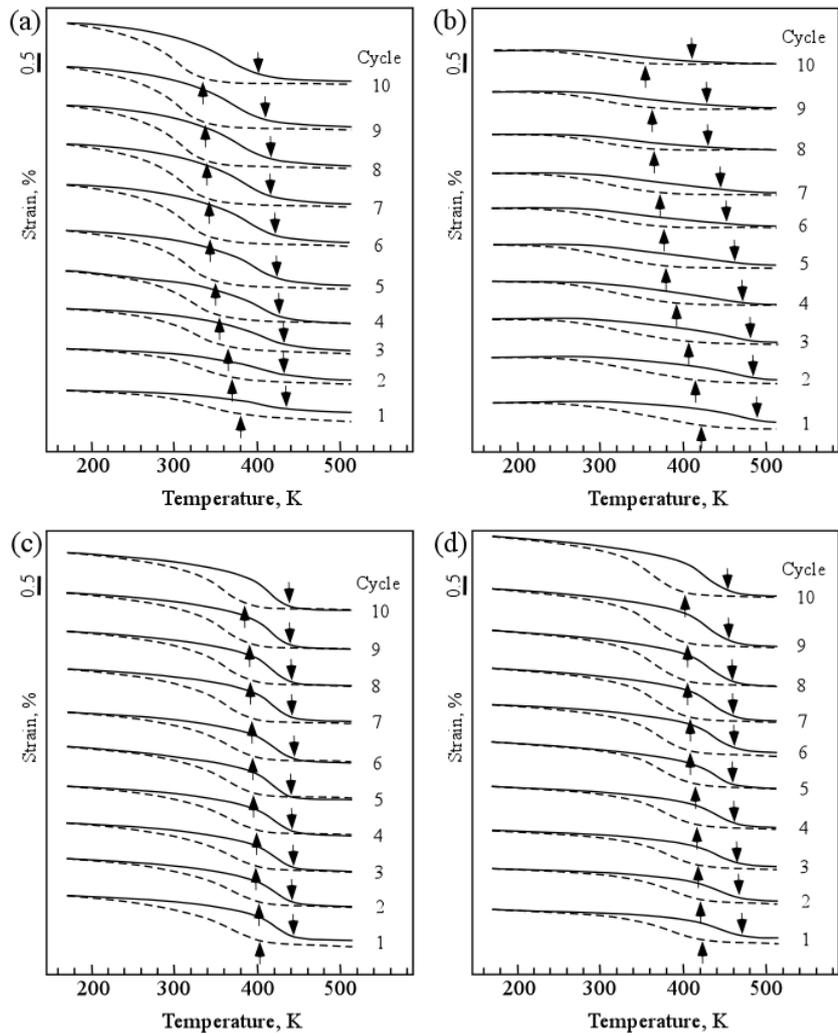cles was 10 K for 1Sn specimen and 18 K for 1Al specimen. As mentioned above the decrease of *Ms* temperature due to aging at 573 K (ΔMs_{aging}) was due to the precipitation of ω phase. The formation of ω phase by aging was not suppressed in 1V and 1Zr specimens, explaining the poor thermal stability of the high temperature shape memory effect. On the other hand the 1Al and 1Sn specimens exhibited stable high temperature shape memory effect since the formation of ω phase was suppressed. For further investigation it is recommended that a more systematic investigation on the effect of Al and Sn addition to Ti-Ta ternary alloys is necessary in order to explore the composition range having stable high temperature shape memory effect and to elucidate the reason why the addition of both elements suppresses the formation of ω phase.
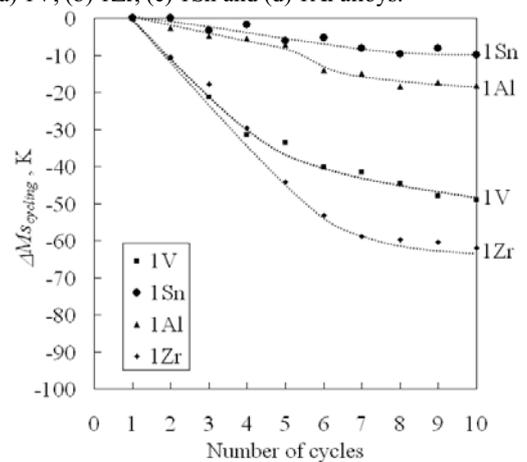

Fig. 9 Strain-temperature curves of (a) 1V, (b) 1Zr, (c) 1Sn and (d) 1Al alloys.

Fig. 10. ΔMs vs. the number of cycles for 1Zr, 1Sn and 1Al alloys.

9. Conclusions

1. The shape memory behavior of Ti-Ta alloys was confirmed for Ti-(30-40)Ta solution treated specimens. The Ms temperature decreased by 30K per 1 at.% Ta. The alloys containing less than 35Ta has Ms temperature above 373K, so they are considered as high temperature shape memory alloys.

2. Stable shape memory effect was confirmed for Ti-32Ta (Ms temperature = 440K) during thermal cycling between 173K and 513K, where Ms temperature did not significantly decreased after five thermal cycles. On the other hand for Ti-22Nb (Ms temperature = 420K) the shape memory effect during thermal cycling exhibited poor stability. For example during thermal cycling between 173K and 513K the shape memory effect was confirmed on the first cycle, but during the second thermal cycle it was completely suppressed. The poor stability of shape memory effect was due to the large amount of ω phase formed in Ti-22Nb when compared with Ti-32Ta.

3. The addition of ternary alloying element (X = V, Cr, Fe, Zr, Hf, Mo, Sn, Al) decreased the Ms temperature of Ti-30Ta. The factors that affect the decrease of Ms temperature due to alloying were the number of valence electrons and the atomic size of the alloying element. The element with a high number of valence electrons and a small atomic size strongly decreased the Ms temperature.

4. The Ms temperature of Ti-30Ta-1X alloys decreased due to aging at 573 K for 3.6 ks. The amount of decrease was more than 100 K for the 30Ta specimen and the decrease of Ms temperature due to aging was caused by the formation of ω phase. The addition of V, Cr, Fe, Zr, Hf and Mo to Ti-30Ta did not suppress the effect of aging on the Ms temperature since they did not suppress the formation of the ω phase during aging treatment. On the other hand the addition of Al and Sn significantly suppressed the effect of aging on the Ms temperature since they suppressed the formation of ω phase during aging treatment.

5. Among the ternary alloys investigated in this study stable high temperature shape memory effect during thermal cycling were identified in Ti-30Ta-1Al and Ti-30Ta-1Sn specimens. In this regard it is suggested that novel Ti-Ta-Al and Ti-Ta-Sn high temperature shape memory alloys are attractive for practical applications.

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