Effect of Aging Treatment on Superelasticity of a $Ti_{48.8}Ni_{50.8}V_{0.4}$ Alloy

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In this study, effect of aging treatment on microstructure, deformation behavior, and superelasticity of $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy was investigated. After aging at 400 °C for 30 min, Ti_3Ni_4 precipitates formed. With increasing aging temperature from 300 to 450 °C, the yield strength of reoriented martensite increased due to the strengthening effect of Ti_3Ni_4 phase, thus improved the shape recovery ratio and reduced the stress hysteresis. Further increasing the aging temperature, the size of Ti_3Ni_4 precipitates increased and the coherency between precipitate and matrix gradually lost, leading to the decreasing yield strength of reoriented martensite and shape recovery ratio. Simultaneously, the stress hysteresis increased resulting from the hinder of plastic deformation to the interfacial movement during phase transformation. The critical stress to induce martensitic transformation continuously decreased with increasing aging temperature.

1. Introduction

As one of the most important properties, superelasticity of TiNi-based shape memory alloys (SMAs) has attracted much attention due to its ability to recover a relatively large deformation during unloading. The superelasticity is related to stress-induced martensitic transformation, which usually occurs in parent phase. Thus, to obtain the stable superelasticity at room temperature, the transformation temperature should be tailored. It is generally accepted that alloying is the most effective method to adjust the transformation temperature of TiNi-based SMAs. The proper addition of vanadium (V) can remarkably lower the transformation temperature. The substitution of 1 at.% V for Ni reduces the martensitic transformation start temperature (M_s) by about 20 °C (Ref 1). Several important aspects of TiNiV alloy, including microstructure, martensitic transformation behavior, and shape memory effect have been reported (Ref 2, 3). Lin et al. (Ref 3) once

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investigated $Ti_{49.25-x/2}Ni_{50.75-x/2}V_x$ (x = 0-4 at.%) alloys and found when the V content is <2 at.%, the transformation temperature decreases with the increasing V content because of solid solution strengthening, and the shape recovery ratio is slightly improved compared to the TiNi binary alloy. If the V content is increased to the range of 2-4 at.%, the transformation temperature increases with the increasing V content (Ref 3).

Aging treatment usually influences the superelasticity of Ni-rich TiNi-based SMAs through the precipitation of Ti_3Ni_4 phase. For example, increasing the aging temperature within 400-600 °C increases the critical stress to induce martensitic transformation, but decreases the yield stress of stress-induced martensite in $Ti_{49.1}Ni_{50.9}$ alloy (Ref 4). It has been reported that after aging at 400 °C, the coherent Ti_3Ni_4 precipitates are observed in $Ti_{47.25}Ni_{48.75}V_4$ alloy (Ref 2). Our group has systematically investigated the effect of aging on martensitic transformation of $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy (Ref 5). After aging for 30 min, the transformation temperatures of $Ti_{48.8}Ni_{50.8}V_{0.4}$ increase with the increase in aging temperature from 300 to 600 °C (Ref 5). Aging at 500 °C for up to 10 h results in a complex multiple-stage transformation upon cooling and heating (Ref 5). This has been ascribed to the effect of Ti_3Ni_4-type precipitates (Ref 5). He and Liu (Ref 6) also investigated the effect of annealing and aging on the martensitic transformation behavior of $Ti_{48.7}Ni_{50.8}V_{0.5}$ alloy and achieved a similar finding with our previous work. However, further detail concerning on the effect of aging process on superelasticity of TiNiV alloy is yet not available. This study is a sequel to our paper previously published (Ref 5) and mainly investigates the effect of aging process on microstructure and superelasticity of $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy.

2. Experimental Procedure

A commercial $Ti_{48.8}Ni_{50.8}V_{0.4}$ (at.%) in rod form was used. The samples were sealed in vacuum quartz tubes and then solution-treated at 900 °C for 2 h followed by quenching into water. The solution-treated samples were then aged in a vacuum

Table 1 Aging temperatures and durations of $Ti_{48.8}$-$Ni_{50.8}V_{0.4}$ alloy

Group	Aging temperature, °C	Aging duration, h
1	300, 350, 400, 450, 500, 550, 600	0.5
2	500	1, 2, 5, 10

for 30 min at various temperatures between 300 and 600 °C (Group 1) and at 500 °C for various durations (Group 2). The detailed aging temperatures and durations are shown in Table 1. After the aging treatment, the samples were slightly polished to remove the surface oxide layer. The microstructure was carefully observed on a Tecnai G2 F30 transmission electron microscope (TEM), which was operated at 300 kV with a double-tilt sample stage. The foils for the TEM were prepared by mechanical grinding, followed by twin-jet electropolishing using an electrolyte solution consisting of 95 vol.% acetic acid and 5 vol.% perchloric acid. The mechanical properties and superplasticity were tested with an Instron 3365 tensile machine equipped with a thermal chamber. The gage length was fixed at 25 mm. The strain rate was 1.3×10^{-4} s^{-1}.

3. Results and Discussion

3.1 Microstructure

Figure 1 shows that the precipitation in the $Ti_{48.8}Ni_{50.8}V_{0.4}$ samples depends on the aging temperature and duration. The microstructure of the solution-treated sample is characterized by a block-like particle with an irregular shape embedded into the matrix. The matrix is parent phase and the particles are $(Ti,V)_2Ni$ phase (Fig. 1a), which agrees well with the previous results (Ref 5). After aging at 300 °C for 30 min, the microstructure is quite similar to that of the solution-treated one. If the aging temperature was increased to 400 °C, a large amount of precipitates with a size of 40-50 nm were observed (Fig. 1b). According to the corresponding SAED pattern shown in Fig. 1(c), they are determined to be Ti_3Ni_4 phase. The same precipitates were also observed in aged $Ti_{47.25}Ni_{48.75}V_4$ alloy (Ref 2). This is different from the XRD result in which no Ti_3Ni_4 precipitate is identified (Ref 5), which is possibly due to their small size. After aged at 500 °C for 30 min, the size of Ti_3Ni_4 precipitate grew slightly to about 100-200 nm (Fig. 1d). The distribution of Ti_3Ni_4 precipitate is not homogeneous. Much more precipitates locate in the region near to the grain boundary. This is naturally reasonable as the grain boundaries may provide the nucleation sites during precipitation. The similar distribution of Ti_3Ni_4 precipitate was also observed in Ni-rich TiNi alloys (Ref 7, 8). Further increasing the aging temperature to 600 °C leads to the growth of the Ti_3Ni_4 precipitate to about 200-300 nm (Fig. 1e). It is seen that the Ti_3Ni_4 precipitates are also clustered around the $(Ti,V)_2Ni$ phase, besides the grain boundary. With increasing the aging temperature, the strain-field contrast around precipitates becomes weak. This indicates that the gradual loss of coherency between precipitate and matrix, agreeing well with the results previously reported (Ref 9). When aged at 500 °C, the precipitate size increases from about 200 to 300 nm with increasing the aging duration from 2 to 10 h, as shown in Fig. 2. The microstructural evolution in $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy is quite similar to that in Ni-rich $Ti_{49.1}Ni_{50.9}$ alloy (Ref 10).

3.2 Superelasticity

Figure 3 shows the room temperature stress-strain curves of the samples subjected to different heat treatments. According to our previous work (Ref 5), all the samples were in the B2 parent phase state. It is seen that the stress-strain curves can be divided into four different stages, as pointed out in the figure, except for the solution-treated sample. This is a general deformation behavior observed in TiNi-based SMAs (Ref 4, 11, 12). In the first stage, the stress increases rapidly, corresponding to the elastic deformation of B2 parent phase. In the second stage, these curves show a clear Lüders-like deformation over a stress plateau, relating to the stress-induced martensitic transformation. The critical stress to induce martensitic transformation is denoted as σ_{SIM}. In the third stage, the stress increases linearly with increasing the strain, corresponding to the elastic deformation of stress-induced martensite. The last stage is related to the plastic deformation. The onset point of this stage is denoted as the yield strength of the oriented martensite (σ_y^M). The σ_y^M of the solution-treated sample was determined from another tensile test (Ref 13) because the present stress-strain curve did not show a clear last stage. It should be pointed out that the sample aged at 500 °C for 30 min shows a two-stage transformation upon cooling (Ref 5). However, the stress-strain curve does not show such a transformation induced by stress. This is possibly because that the first transformation is too weak to be detected by tensile testing.

Figure 4 shows the dependences of σ_y^M and σ_{SIM} on aging treatment. It is seen that these two critical stresses show the different tendency with aging treatment, which is quite similar to that observed in aged $Ti_{49.1}Ni_{50.9}$ alloy (Ref 4). The effect of aging treatment on σ_y^M can be related to the precipitate evolution. When the aging temperature was 300 °C, no Ti_3Ni_4 precipitates were observed. Therefore, the σ_y^M did not show obvious change. With increasing the aging temperature to a temperature between 400 and 450 °C, the microstructure is characterized by the densely distributed Ti_3Ni_4 precipitates, which are coherent with the matrix. This is confirmed by the results shown in Fig. 1(b). This is responsible for the increase of resistance to dislocation movement, i.e., the increase of σ_y^M. When the aging temperature was further increased to 600 °C, the coherency between Ti_3Ni_4 precipitates and matrix gradually lost and the distance between the precipitates increased. Therefore, the strengthening effect becomes weak and the σ_y^M decreases. When aged at 500 °C, the distribution of precipitates becomes homogeneous with increasing aging duration from 30 min to 10 h. This should be responsible for the increase of σ_y^M shown in Fig. 4(b).

Our previous results (Ref 5) show that with increasing aging temperature or duration, the transformation temperatures of aged $Ti_{48.8}Ni_{50.8}V_{0.4}$ continuously increases. This agrees well with the decrease in σ_{SIM} with increasing aging temperature or duration, as shown in Fig. 4. The similar results have been reported in aged $Ti_{49.1}Ni_{50.9}$ alloy and $Ti_{49.3}Ni_{50.8}V_{0.5}$ alloy (Ref 4, 14).

Figure 5 shows the typical stress-strain curves of the $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloys. Cyclic tests were performed at room temperature. One sample was, respectively, deformed to 2, 4, 8, 10, and 16% strains. For the solution-treated sample, partial superelasticity is observed in the first three cycles, as shown in Fig. 5(a). Both the residual strain and the shape recovery strain after unloading increase progressively as cycling proceeds. When the deformation strain is larger than 10%, the stress-plateaus
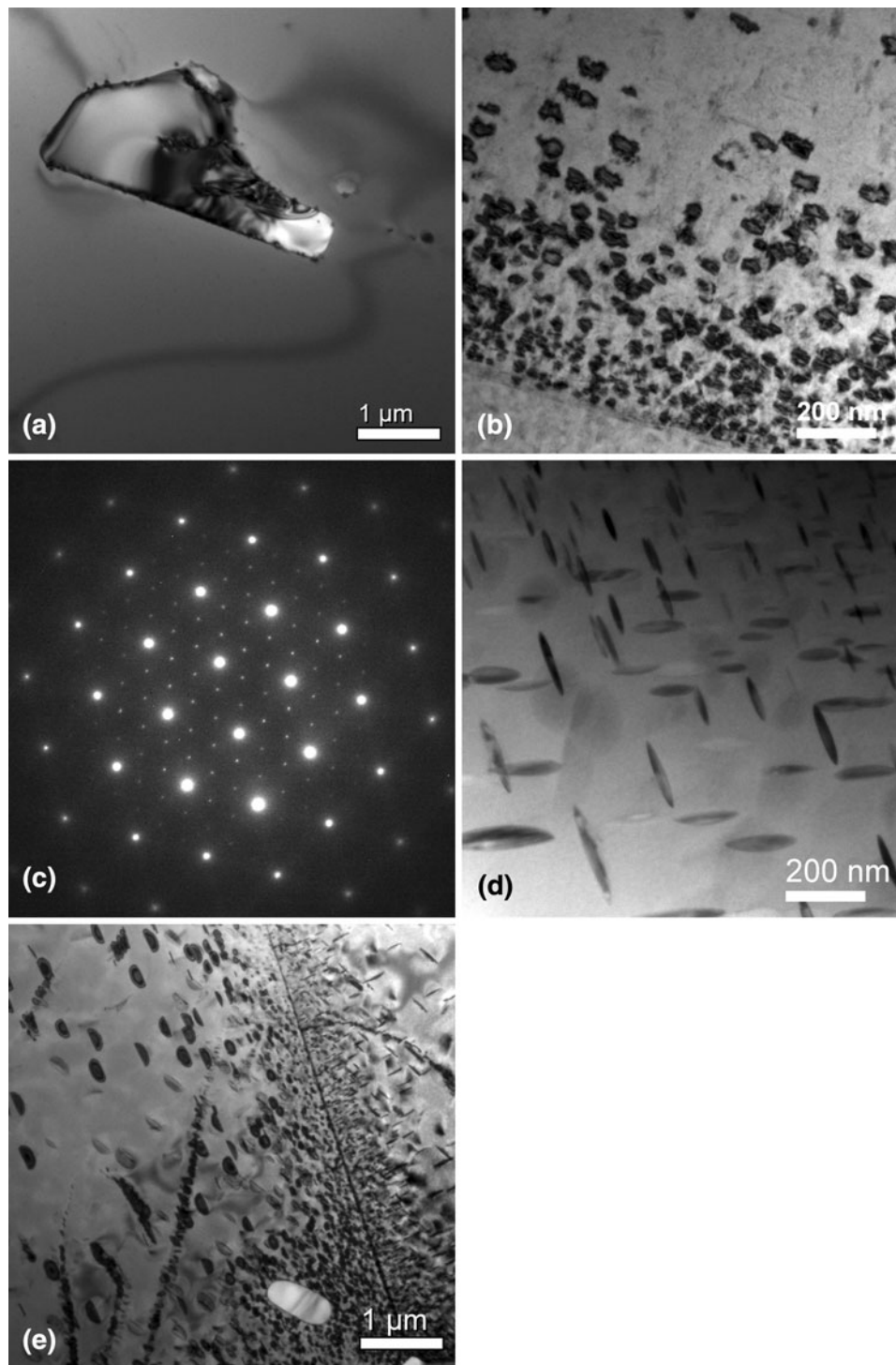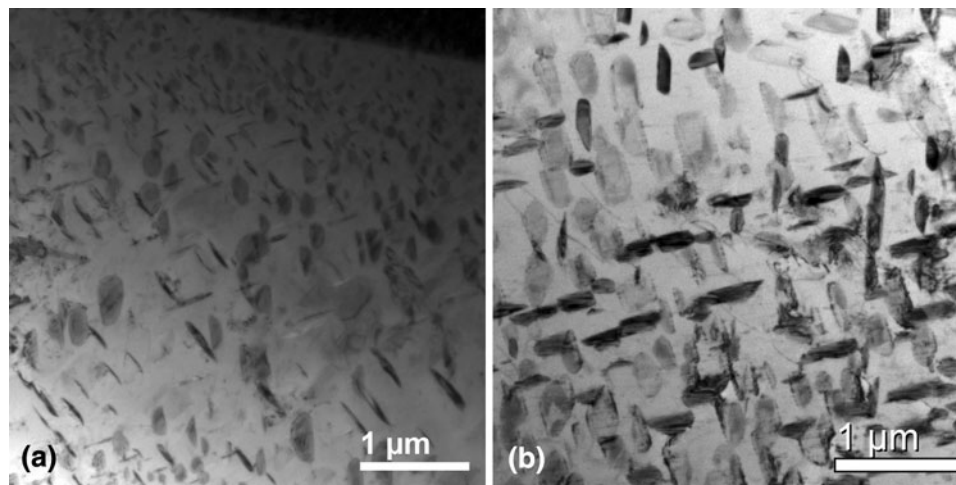
Fig. 1 TEM images of the solution-treated $Ti_{48.8}Ni_{50.8}V_{0.4}$ sample (a) and the samples aged at different temperatures for 30 min, 400 °C (b), 500 °C (c), and 600 °C (d).The electron in (e) was taken from sample (b). The incident beam is parallel to $[111]_{B2}$

associated with the reverse transformation of stress-induced martensitic transformation almost disappear. Figure 5(b) shows the stress-strain curves for the sample aged at 500 °C for 30 min. The stress-plateaus related to the stress-induced martensitic transformation, and corresponding reverse transformation can be easily identified at the loading process of every cycle, though no obvious recovery was identified in the last unloading process. The sample shows a near-perfect superelas-

ticity at the first two cycles when the deformation strain is below 4%. Figure 5(c) shows the stress-strain curves of the sample aged at 500 °C for 5 h. It is seen that the sample does not show an obvious stress-plateau during unloading. Previous work (Ref 5) shows that the sample is of parent phase at room temperature, and its reverse transformation finish temperature is very close to the room temperature. Thus, it is possible that the unloading process does not provide a sufficient driving force
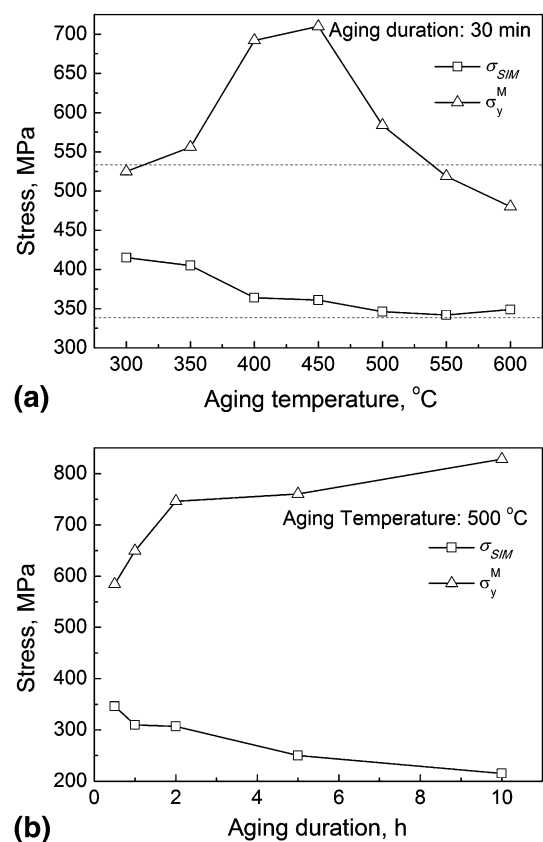
Fig. 2 TEM images of the $Ti_{48.8}Ni_{50.8}V_{0.4}$ samples aged at 500 °C for 2 h (a) and 10 h (b)
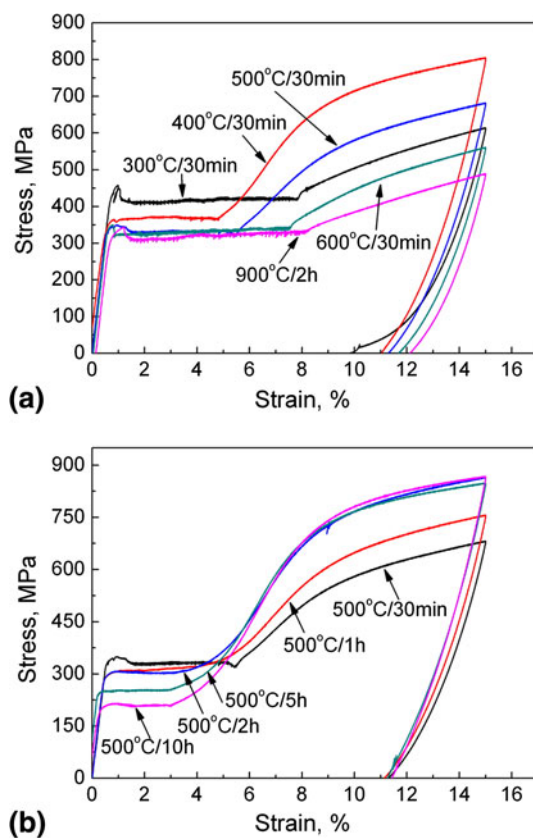
Fig. 3 Stress-strain curves of the TiNiV alloys solution-treated and aged at different temperatures for 30 min (a) and at 500 °C for different durations (b). The testing temperature was room temperature

Fig. 4 Effects of aging temperature (a) and duration (b) on σ_y^M and σ_{SIM}. The data of the solution-treated sample are also given as dashed line

for martensite to parent phase at room temperature, resulting in the absence of stress-plateau. Further increase of aging duration shows the similar stress-strain curves. In the following, we no longer discuss the effect of aging duration on superelasticity at room temperature.

The effect of aging temperature on the recovery ratio of aged samples is shown in Fig. 6(a). The deformation strain is 4%. The recovery ratio is defined as the ratio of superelasticity
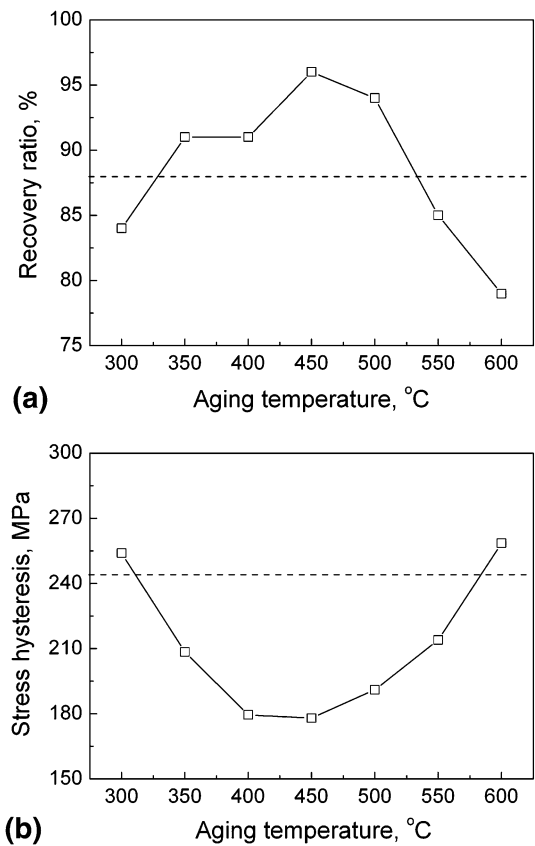
recovery strain to deformation strain. The recovery ratios show the similar dependence on aging temperature under other deformation strains. When aged at a temperature between 350 and 500 °C, the samples show larger recovery ratio than the solution-treated sample. When the aging temperature is below 450 °C, the recovery ratio increases with increasing the aging temperature. Further increase of the aging temperature results in the decrease of the recovery ratio. The superelasticity of the
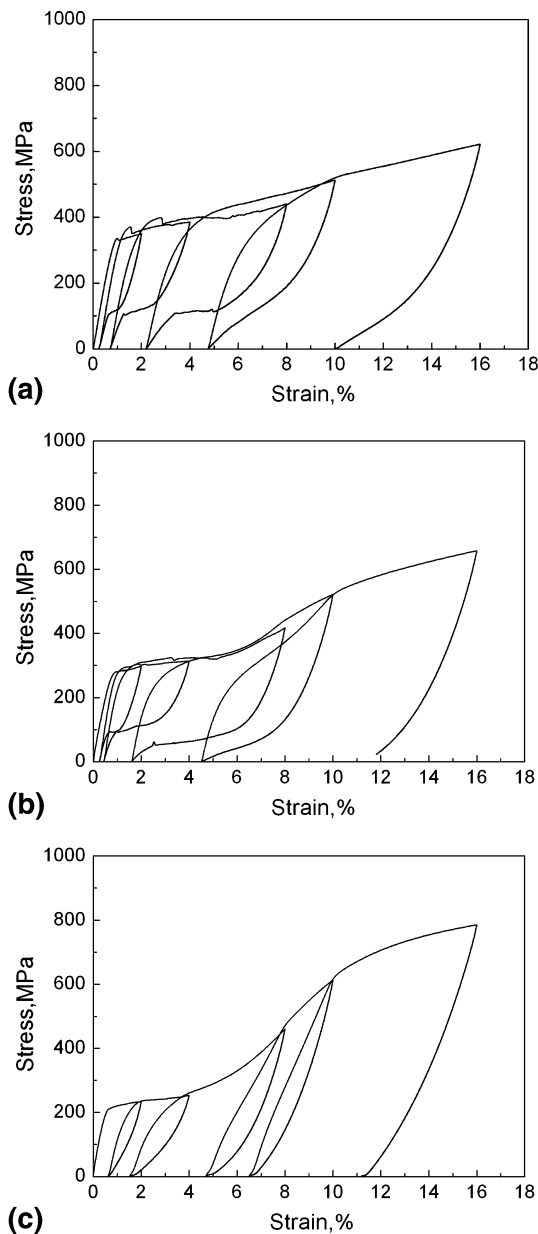
Fig. 5 Typical stress-strain curves from cycle deformation of the solution-treated sample (a), the sample aged at 500 °C for 30 min (b) and 500 °C for 5 h (c). The testing temperature was room temperature


Fig. 6 Effect of aging temperature on the recovery ratio (a) and the stress hysteresis (b). The data of the solution-treated sample are also given as dashed line

present alloys is less than that of the solution-treated $Ti_{49.4}Ni_{50.6}$ alloy which shows a full recovery until the deformation strain is 8% (Ref 15) and $Ti_{49.15}Ni_{50.85}$ alloy (Ref 16) and TiNiCuCr alloy (Ref 17, 18). According to the results shown in Fig. 6, it is proposed that aging at 450 °C for 30 min is the optimum process to obtain excellent superelasticity in $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy at room temperature.

Figure 6(b) shows the stress hysteresis as a function of aging temperature. The stress hysteresis is defined as the difference between the plateau stress of forward and reverse transformation when the strain is 2%. When the aging temperature was below 450 °C, the stress hysteresis decreases with increasing aging temperature. The sample aged at 450 °C shows the minimum hysteresis of 167 MPa. Further increase in the aging temperature leads to the increase of stress hysteresis.

As compared to the stress hysteresis of the solution-treated sample, all the samples show the lower value except for the samples aged at 300 and 600 °C. It is also seen from Fig. 5 that the stress hysteresis increases with the increasing deformation strain. The same dependence of stress hysteresis on deformation strain was also observed in other TiNi-based SMAs (Ref 19).

The dependences of recovery ratio and stress hysteresis on aging temperature can be related to the critical stress for slip. In this study, the exact value of critical stress for slip is unknown. However, this stress usually show the same tendency with the σ_y^M. It is suggested that when the aging temperature is below 450 °C, the critical stress for slip reaches the maximum value due to the precipitation strengthening of Ti_3Ni_4 phase. Correspondingly, the recovery ratio shows the maximum value (Fig. 6a) as the minimum plastic deformation is introduced. The effect of aging temperature on stress hysteresis (Fig. 6b) is opposite to that on recovery ratio (Fig. 6a), indicating that the stress hysteresis is closely related to the plastic deformation or residual strain. This is reasonable as that the residual strain may increase the frictional work against the interfacial movement during phase transformation through the dislocation generation and movement.

Figure 7 shows the stress-strain curves of $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloys after solution and aging treatment. The deformation temperature was increased to 40 °C. The deformation strain was 8%. From Fig. 7(a), it is seen that most of the samples do not show the obvious stress-plateau during unloading except for the sample aged at 400 °C for 30 min. This is due to the
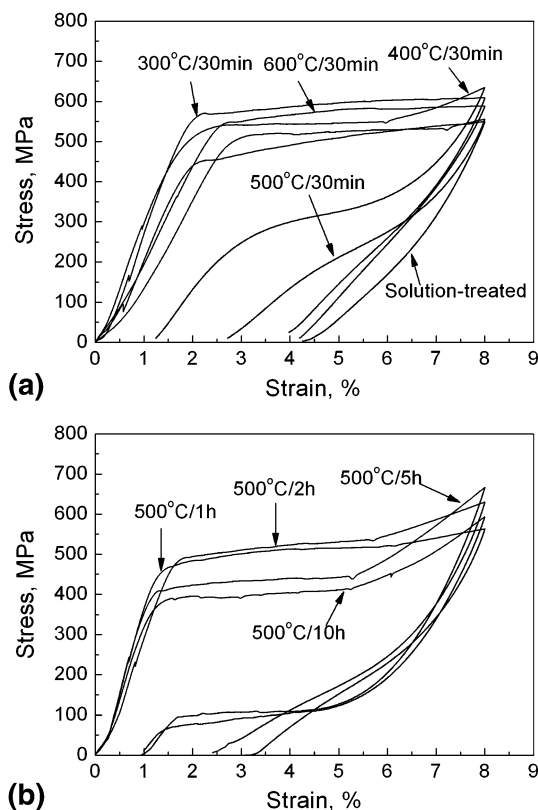
Fig. 7 Stress-strain curves of the TiNiV alloys solution-treated and aged at different temperatures for 30 min (a) and at 500 °C for different durations (b). The testing temperature was 40 °C

introduction of plastic deformation during loading. Figure 7(b) shows that for the samples aged at 500 °C for different durations, the superelasticity loop becomes clear with increasing aging duration, resulting from the increased yield stress. This is confirmed by the results shown in Fig. 4. If the deformation temperature was further increased to 60 °C, all the stress-strain curves do not show the clear superelasticity loop except for the samples at 500 °C for 5 and 10 h. This indicates that the utilizing temperature of superelasticity in $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy should be below 60 °C.

4. Conclusions

(1) After aging at 400 °C for 30 min, Ti_3Ni_4 precipitates form in $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy. With increasing aging temperature or duration, the size of precipitate grows.

(2) The yield strength of the oriented martensite and critical stress to induce martensitic transformation both depends on the aging treatment. With increasing aging temperature to 450 °C, the yield strength reaches the maximum value due to the effect of Ti_3Ni_4 precipitates. The critical stress to induce martensitic transformation continuously decreases with increasing aging temperature.

(3) When aged at different temperatures for 30 min, the recovery ratio increases with the increasing aging temperature from 300 to 450 °C. Further increase of aging temperature leads to the decrease of recovery ratio. The stress hysteresis shows the opposite dependence on the aging temperature.

(4) The aged $Ti_{48.8}Ni_{50.8}V_{0.4}$ alloy shows the well-defined superelasticity when the deformation temperature is below 60 °C.

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