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Effect of aging on martensitic transformation and superelasticity of TiNiCr shape memory alloy

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Abstract: The effect of aging on microstructure, martensitic transformation and superelasticity of a $Ti_{48.4}Ni_{51.1}Cr_{0.5}$ alloy was investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) analysis and tensile tests. When the alloy was aged at 400 °C for 30 min, Ti_3Ni_4 precipitate appears. When aged at a temperature between 400 °C and 500 °C, the samples show a two-stage martensitic transformation. The aged $Ti_{48.4}Ni_{51.1}Cr_{0.5}$ alloy exhibits a well-defined superelasticity at room temperature. The recovery ratio increases with 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 aging temperature. The relationship between aging treatment and martensitic transformation and superelasticity can be rationalized by the evolution of Ti_3Ni_4 precipitate.

Key words: TiNiCr; shape memory alloy; Ti₃Ni₄ precipitate; martensitic transformation; superelasticity; aging

1 Introduction

TiNi shape memory alloys (SMAs) have been widely used in biomedical applications due to their unique shape memory effect (SME), superelasticity and good biocompatibility [1,2]. The superior properties of TiNi SMAs are related to martensitic transformation which can be thermally-induced or stress-induced [3]. In order to tailor martensitic transformation and mechanical properties of SMAs for a specific purpose, alloying of the third element is a common and effective method. The addition of Cr has attracted much attention because it not only adjusts the transformation temperatures [3], but also results in improvements of mechanical properties, such as yield stress [4], torqueability and stiffness [5], fatigue life [6]. The above results promote the applications of TiNiCr alloys in the biomedical field as retriever devices, dental and guide wires [6].

To date, several important aspects of TiNiCr alloys have been reported, including martensitic transformation [5,7,8], mechanical properties [6,9,10] and superelasticity [10]. It is now well accepted that the addition of Cr lowers the transformation temperatures [5]. Depending on the composition, the solution-treated TiNiCr alloys may exhibit a two-stage parent phase $(A) \rightarrow R$ -phase $(R) \rightarrow martensite (M)$ transformation upon Ti₅₀Ni_{49.5}Cr_{0.5} cooling [7]. For example, and $Ti_{51}Ni_{48.5}Cr_{0.5}$ alloys show a two-stage $A \rightarrow R \rightarrow M$ transformation upon cooling and a $M \rightarrow A$ transformation upon heating [7]. The transformation behavior is also dependent on the thermo-mechanical treatment. After 45% cold deformation, only $A \rightarrow R$ transformation is observed upon cooling [8].

The addition of Cr increases the critical stress to induce martensitic transformation and yield stress due to the solution-strengthening [4,7], resulting in the increased SME [7]. CHOI and NEMAT-NASSER [10] investigated the mechanical response of a $Ti_{47.09}Ni_{52.62}$ - $Cr_{0.29}$ alloy as a function of annealing temperature and deformation temperature by compressive tests, and reported that the critical stress to induce martensitic transformation and critical stress for slip decrease with increasing annealing temperature from 300 to 500 °C.

It is generally accepted that superelasticity is related to the stress-induced martensitic transformation and its

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reverse transformation [2], implying that this behavior can only take place in parent phase. In order to obtain a stable superelasticity, the TiNi-based SMAs are usually Ni-rich. They are essentially influenced by aging treatment because of precipitation of Ti₃Ni₄ phase. It was reported that after annealing between 300 and 500 °C for 1 h, Ti₃Ni₄ precipitates are visible in a hot-rolled Ni_{52.62}Ti_{47.09}Cr_{0.29} alloy [10]. The effect of aging treatment on martensitic transformation and deformation behavior of Ni-rich binary TiNi SMAs has been well understood [11–14]. However, the findings in TiNi binary alloys cannot be directly applied to TiNiCr ternary alloy since the effect of aging is processing and compositional dependent.

The purpose of this work is to provide a systematical investigation on the effect of aging treatment on martensitic transformation and superelasticity of a $Ti_{48,4}Ni_{51,1}Cr_{0.5}$ alloy. Based on the experimental results, this effect is discussed in terms of precipitate evolution.

2 Experimental

2.1 Sample preparation

A commercial $Ti_{48.4}Ni_{51.1}Cr_{0.5}$ (mole fraction, %) alloy in rod form was used. After removing the surface oxide, 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 for 0.5 h at various temperatures between 300 and 600 °C. After the aging treatment, the samples were slightly mechanically polished to remove the surface oxide layer again.

2.2 Microstructure observation and phase analysis

Phase constitution was determined by X-ray diffraction (XRD) at room temperature. The tests were carried out on a PANalytical Xpert'pro diffractometer at room temperature using Cu K_a radiation. The scanning range is from 10° to 100° at intervals of 0.02° with a stepping time of 4 s. Transmission electron microscopy (TEM) observations were carried out on a Tecnai G2 F30 operated at 300 kV with a double-tilt specimen stage. Thin foils for TEM observations were prepared by a twin-jet electropolishing in an electrolyte solution consisting of 95% acetic acid and 5% perchloric acid by volume.

2.3 Martensitic transformation behavior analysis

Martensitic transformation behavior was characterized using a Perkin-Elmer diamond differential scanning calorimeter (DSC) with a heating and cooling rate of 20 °C/min. In order to ensure a good resolution, the mass of the samples was 10-20 mg.

2.4 Mechanical and superelasticity characterization

Tensile tests were carried out on an Instron 3365 materials testing machine equipped with a thermal chamber. Superelastic behavior was measured by cyclic loading–unloading tensile tests. During the tests, one sample was first deformed to 2%, and then unloaded. The measurement was repeated by increasing the strain to 4%, 8%, 10% and 16%, respectively. The gauge 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(a) shows the XRD patterns of solutiontreated and aged samples measured at room temperature. Figure 1(b) shows the locally enlarged graph of Fig. 1(a). From Fig. 1(a), it can be seen that the phase constitution in TiNiCr alloy samples depends on aging temperature. When solution-treated at 900 °C for 2 h, the sample consists of B2 parent phase and Ti₂Ni-type phase. The formation of Ti₂Ni-type phase is possibly due to the introduction of oxygen during melting [15], which will not be discussed hereafter. After aging at 500 °C for 30 min, the peaks corresponding to Ti₃Ni₄ precipitate started to appear, as shown in Fig. 1(b).

In order to further understand the precipitation behavior in TiNiCr alloy samples, TEM observation was carried out. The microstructure of the solution-treated sample is characterized by a block-like particle with an irregular shape embedded into the matrix (Fig. 2(a)). The particles are believed to be Ti₂(Ni,Cr) phase [7]. 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 number of precipitates with a size of less than 50 nm are observed (Fig. 2(b)). It is seen that the pattern is characterized by the 1/7 superlattice spots in the $\langle \overline{2}\overline{1}3 \rangle$ direction, indicating the presence of Ti₃Ni₄ phase. This is different from the XRD result in which no Ti₃Ni₄ precipitate is identified, which is possibly due to the small size. The distribution of Ti₃Ni₄ precipitate is not homogeneous. Much more precipitates locate in the region near the grain boundary and around the Ti₂(Ni,Cr) phase. This is naturally reasonable since the grain boundary and the interface between Ti₂(Ni,Cr) phase and matrix may provide the nucleation sites during precipitation. The similar distribution of Ti₃Ni₄ precipitate was also observed in Ni-rich TiNi alloys [11,12]. The R-phase can also be recognized by weak diffraction spots occurring at $1/3(110)_{B2}$ positions, as indicated by the white arrows in the inset of Fig. 2(b). Further increasing the aging temperature to 600 °C leads to the growth of the Ti₃Ni₄



Fig. 1 XRD patterns of samples solution-treated and aged at different temperatures for 30 min



Fig. 2 TEM bright field images of samples solution-treated (a) and aged at 400 °C (b), 500 °C (c) and 600 °C (d) for 30 min (The corresponding SAED patterns are also inserted)

precipitate to (250 ± 50) nm (Fig. 2(d)). The diffraction spots corresponding to Ti_3Ni_4 precipitate are not observed. This possibly results from the loss of coherency between precipitate and matrix [16]. With increasing the aging temperature, the strain-field contrast around precipitates becomes weak.

3.2 Martensitic transformation

Figure 3 shows the DSC curves of the solution-

treated sample and the samples aged at different temperatures for 30 min. The solution-treated sample shows a single-stage transformation behavior upon cooling and heating. The transformation temperatures are below room temperature, which is consistent with the XRD result shown in Fig. 1. The samples aged at 300 °C and 350 °C undergo a single-stage transformation behavior upon cooling and heating. The samples aged between 400 and 500 °C clearly show a two-stage

reverse transformation upon heating, as indicated by the arrows. With further increasing aging temperature, the transformation behavior is characterized by a single-stage transformation behavior upon cooling and heating.



Fig. 3 DSC curves of samples solution-treated and aged at different temperatures for 30 min

In order to identify the transformation peaks of the samples aged between 400 and 500 °C, the partial DSC technique was used [11]. This method requires heating to 40 °C, and holding for 2 min to obtain the parent phase state; cooling to a predefined temperature and holding for 2 min before heating. The full cycle of the sample aged at 500 °C is shown in Fig. 4(a). First, the end temperature of cooling is set between peak 1 and peak 2 (Fig. 4(b)). A weak peak at the position of peak 2' is observed during heating. The hysteresis between peak 1 and 2' is about 4.5 °C, thus this pair results from the reversible R phase transformation. The results in Fig. 4 indicate that the samples aged between 400 and 500 °C undergo a $A \leftrightarrow R \leftrightarrow M$ transformation upon cooling and heating.



Fig. 4 Partial DSC curves of sample aged at 500 °C for 30 min (The original full DSC curve of this sample is shown in Fig. 4(a))

Figure 5 shows the dependence of transformation temperature on aging temperature. The horizontal dashed-lines represent the transformation temperatures of the solution-treated sample. $M_{\rm s}$, $M_{\rm p}$, $M_{\rm f}$, $A_{\rm s}$, $A_{\rm p}$ and $A_{\rm f}$ are martensitic transformation start temperature, martensitic transformation peak temperature, martensitic transformation finish temperature, reverse martensitic transformation start temperature, reverse martensitic transformation peak temperature and reverse martensitic transformation finish temperature, respectively. R_{As} , R_{Ap} and RAf are reverse R-phase transformation start temperature, reverse R-phase transformation peak temperature and reverse R-phase transformation finish temperature, respectively. As compared to the solutiontreated sample, the aged samples show lower transformation temperatures if the aging temperature is below 500 °C, after that, they show higher transformation temperatures. According to the effect of aging temperature on transformation behavior, the samples aged at different temperatures for 30 min can be divided into three groups, as shown in Fig. 5. The first group includes the samples aged at a temperature below 400 °C, in which the M_s temperature decreases with increasing the aging temperature. The second group consists of the samples aged between 400 and 500 °C. The transformation behavior of this group is characterized by a $A \leftrightarrow R \leftrightarrow M$ two-stage transformation the continuously increased transformation and temperature with the aging temperature. The samples aged at a temperature higher than 550 °C belong to the third group in which the transformation temperatures continuously increase with the aging temperature. It should be emphasized that the symbol of M_s of the second group represents the starting temperature of $R \rightarrow M$ transformation in the second stage, different from the meaning in other two groups in which it corresponds to the starting temperature of $A \rightarrow M$ transformation.



Fig. 5 Effect of aging temperature on transformation temperatures

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The effect of aging temperature on transformation behavior can be ascribed to the influence of precipitation. In the first group, the transformation temperature was suppressed by the aging. This is similar to the dependence observed in a Ti_{49.1}Ni_{50.9} alloy reported in a previous work in which this suppression was assumed to be due to the atomic rearrangement as a precursor for precipitation [17]. In order to confirm this assumption, a HRTEM observation was carried out on the sample aged at 300 °C. The result is shown in Fig. 6. It is seen that the microstructure is characterized by the lattice distortion at nanometer scale, as indicated by the white arrows. The lattice distortion regions not only act as the nucleation sites for the subsequent precipitation of Ti₃Ni₄ phase, but also disturb the level of ordering of the B2 matrix and then result in the decrease in transformation temperature. In the second group, the two-stage transformation is generally related to the stress field around the coherent Ti₃Ni₄ precipitates [11,17,18]. In the third group, the Ti₃Ni₄ precipitates lose the coherency with the matrix, as shown in Fig. 2(d). This results in the single-stage transformation. The depletion of Ni content resulting from the precipitation should be responsible for the continuously increased transformation temperature with increasing aging temperature in the second and third groups.



Fig. 6 HRTEM image of sample aged at 300 °C

3.3 Superelasticity

Figure 7(a) shows the room temperature stressstrain curves of the samples subjected to different heat treatments. According to the results in Figs. 1 and 3, all the samples are in the B2 parent phase state at room temperature. The stress-strain curves can be divided into four different stages, as indicated in the figure. This is a general deformation behavior observed in TiNi-based SMAs [13,19]. During the deformation. the stress-induced martensitic transformation occurs, as evidenced by the stress-plateau. The yield strength of the oriented martensite (σ_v^M) is crucial to understand the



Fig. 7 Typical tensile stress-strain curves of samples aged at different temperatures for 30 min (a) and effect of aging temperature on σ_y^M (b) (The deformation was performed at room temperature)

deformation behavior. Figure 7(b) shows the dependence of $\sigma_{\rm v}^{\rm M}$ on aging temperature. The critical stress of the solution-treated sample is also given in dashed-line. All of the aged samples show larger σ_v^M than the solution-treated one. The sample aged at 450 °C shows the maximum value of σ_y^M . The dependence of σ_y^M on aging treatment is similar to the previously reported results on the hot-rolled Ni52.62Ti47.09Cr0.29 annealed at various temperatures for 1 h [10]. This is related to the microstructural evolution. When the sample is aged at 300 °C, the lattice distortion at nanometer scale as a pre-phenomenon for precipitation results in the slight increase of σ_{v}^{M} . With increasing aging temperature to 400 °C, the coherent Ti₃Ni₄ precipitates appear, as shown in Fig. 2, which is beneficial to increasing the resistance to dislocation movement. Therefore, the $\sigma_v^{\rm M}$ increases with increasing aging temperature. Further increasing aging temperature results in the gradual loss of the coherency between Ti₃Ni₄ precipitates and matrix and the increased distance between the precipitates. Therefore, the strengthening effect becomes weak and the σ_v^M decreases.

Figure 8 shows the typical stress-strain curves of the sample aged at 450 °C. Cyclic tests were carried out at room temperature. One sample was deformed to 2%, 4%, 8%, 10% and 16% strains. When the deformation strain is less than 8%, all the samples exhibit superelasticity. Both the residual strain and the recovery strain upon unloading progressively increase as cycling proceeds. When the deformation strain is larger than 10%, the strain-plateau related to the reverse transformation of stress-induced martensitic transformation during unloading almost disappears.



Fig. 8 Typical stress-strain curves from cycle deformation of samples aged at 450 °C for 30 min (The deformation was performed at room temperature)

In the present work, the shape recovery ratio is defined as the ratio of recovery strain to deformation strain, as shown in Fig. 8. The effect of aging temperature on the recovery ratio of the aged samples is shown in Fig. 9. The deformation strain is 4%. The recovery ratio shows the similar dependence on aging temperature under a deformation strain less than 8%. When the sample is aged at a temperature below 450 °C, the recovery ratio increases with increasing aging temperature. Further increase of the aging temperature leads to the decrease of the recovery ratio. In the present work, when the aging temperature is lower than 450 °C, the $\sigma_{\rm v}^{\rm M}$ increases with increasing aging temperature, due to the precipitation strengthening of Ti₃Ni₄ phase, as confirmed by the results in Fig. 7(b). Accordingly, the shape recovery ratio shows the maximum value as the minimum plastic deformation is introduced when the sample is aged at 450 °C. When the deformation strain is 10%, the recovery ratio shows a general decrease with the increase of aging temperature. This indicates that the deformation strain should be less than 10% when the aged $Ti_{48,4}Ni_{51,1}Cr_{0,5}$ is used.

The effect of aging temperature on the stress hysteresis is also shown in Fig. 9. The stress hysteresis is defined as the difference between the plateau stress of



Fig. 9 Effect of aging temperature on recovery ratio and stress hysteresis of samples aged at different temperatures for 30 min (The deformation strain is 4%)

forward and reverse transformation when the deformation is 4%. When the aging temperature is lower than 450 °C, the stress hysteresis decreases with increasing aging temperature. After that, the stress hysteresis increases continuously as the aging temperature increases. The similar dependence of stress hysteresis on aging temperature was also observed in other TiNi-based SMAs [20,21]. Compared with the results on the recovery ratio, it is seen that the dependence of stress hysteresis on aging temperature is opposite to that of recovery ratio, indicating that the stress hysteresis is closely related to the plastic deformation. This is naturally reasonable since the plastic deformation may increase the frictional work against the interfacial movement during phase transformation.

Figure 10 shows the stress-strain curves of the samples after solution and aging treatments. The deformation temperature was increased to 40 °C and the deformation strain was fixed at 8%. It is seen that most of the samples do not show the obvious stress-plateau upon unloading, except for the sample aged at 450 °C for 30 min, consistent with the results shown in Fig. 7(b). This is possibly due to the lower σ_y^M of other samples which fails to effectively prevent the introduction of plastic deformation. This indicates that the aged Ti_{48.4}Ni_{51.1}Cr_{0.5} alloy samples should be utilized at a temperature below 40 °C.

4 Conclusions

1) After aging at 400 °C for 30 min, Ti_3Ni_4 precipitate appears. With increasing aging temperature, the size of precipitate grows. The precipitate mainly distributes along grain boundary or around $(Ti,Cr)_2Ni$ phase.



Fig. 10 Stress-strain curves of samples solution-treated and aged at different temperatures for 30 min (The deformation strain is 8% and the deformation temperature is 40 °C)

2) The transformation behaviors of the samples solution-treated and aged at a temperature below 400 °C are characterized by a single-stage A \leftrightarrow M transformation upon cooling and heating. When the samples are aged at a temperature between 400 °C and 500 °C, the

 $A \leftrightarrow R \leftrightarrow M$ transformation occurs upon cooling and heating due to the precipitation of Ti₃Ni₄ phase. When aging temperature is above 500 °C, only the $A \leftrightarrow M$ transformation is found. The M_s first decreases with increasing aging temperature to 400 °C and then increases with further increasing aging temperature.

3) The aged $Ti_{48.4}Ni_{51.1}Cr_{0.5}$ alloy exhibits the well-defined superelasticity at room temperature. The recovery ratio increases with increasing the 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. This is due to the evolution of Ti_3Ni_4 precipitate with aging temperature. The optimized superelasticity can be obtained through aging at 450 °C that produces fine Ti_3Ni_4 phase to strengthen the matrix.

4) The utilization temperature of superelasticity in aged $Ti_{48,4}Ni_{51,1}Cr_{0,5}$ sample should be below 40 °C.

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时效对 TiNiCr 形状记忆合金马氏体相变与超弹性的影响

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摘 要:通过 X 射线衍射分析(XRD)、透射电子显微观察(TEM)、差式扫描量热分析(DSC)与拉伸实验研究时效 处理对 Ti_{48.4}Ni_{51.1}Cr_{0.5} 合金显微组织、马氏体相变与超弹性的影响规律与机制。经 400 ℃ 时效处理 30 min 后,合 金中形成 Ti₃Ni₄析出相。当时效温度介于 400 ℃ 和 500 ℃ 之间时,合金表现出两步马氏体相变。经时效处理的 Ti_{48.4}Ni_{51.1}Cr_{0.5} 合金在室温下表现出优异的超弹性。随时效温度自 300 ℃ 升高到 450 ℃,超弹性恢复率增加。继 续升高时效温度,恢复率下降。超弹性应力滞后表现出相反的变化趋势。通过分析 Ti₃Ni₄析出相随时效处理的演 化规律解释了时效处理与马氏体相变和超弹性之间的关系。

关键词: TiNiCr; 形状记忆合金; Ti₃Ni₄析出相; 马氏体相变; 超弹性; 时效