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Effect of one variant of Ti_3Ni_4 particles on stress-induced martensitic transformations in <111>-oriented $Ti_{49.2}Ni_{50.8}$ single crystals

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Abstract. In the present study the effects of stress-assisted aging of the $Ti_{49.2}Ni_{50.8}$ single crystals oriented along $[\bar{1}11]$ direction on the stress-induced B2-R-B19′ thermoelastic martensitic transformations and superelasticity are investigated. It is experimentally established that aging at 823 K for 1h under compression stress of 150 MPa along $[\bar{1}11]$ direction leads to the precipitation of one crystallographic variant of Ti_3Ni_4 particles of 350(±30) nm in size. Precipitation the single variant of Ti_3Ni_4 particle results in an appearance of homogeneous long-range internal stress field $|\langle\sigma_G\rangle| \approx 65$ MPa, that defines the main features of stress-induced B2-R-B19′ transformation and determines the increase in the characteristic temperatures of martensitic transformation and the existence of two-way shape memory effect.

1. Introduction

It is known [1-3], that in the widely used Ni-rich alloys of TiNi ($C_{Ni} \geq 50.6$ at. %) the control of the temperatures of thermoelastic B2-R-B19′ martensitic transformation, strength properties of high temperature B2-phase, shape memory effect and superelasticity is achieved by the precipitation of the Ti_3Ni_4 disperse particles from 10 up to 500 nm in size during the ageing in the temperatures interval from 623 to 823 K. The Ti_3Ni_4 disperse particles have a lenticular form with a habit plane of $\{111\}_{B2}$ and do not undergo martensitic transformation [1]. Thus so-called nanocomposites are formed in which the matrix undergoes martensitic transformation, but dispersed particles deform only elastically.

Stress-free ageing results in the precipitation of four crystallographic equivalent variants of particles with four habit plane of $\{111\}_{B2}$ [1-3].The crystallographic variants of Ti_3Ni_4 particles are equivalent in stress-free aged crystals. By contrast, at the aging under uniaxial tensile or compressive stress the crystallographic variants of Ti_3Ni_4 particles possess different elastic energy. Therefore during stress-assisted aging particle variations with low elastic energy should precipitate, and the growth of high energy particle variations will be suppressed. Ideally, only one particle variant oriented in a certain way to the axis of the applied stress should form in stress-assisted single crystals oriented along the $[\bar{1}11]_{B2}$ direction [4]. At the ageing under tensile stress of $[\bar{1}11]$-oriented single crystal the habit plane of Ti_3Ni_4 particles tends to be parallel to the tensile axis and under a compression stress it tends to be perpendicular to the compressive axis. Up to the present the theoretical energy-based approaches for TiNi single crystals and the experimental confirmations of the oriented growth of Ti_3Ni_4 particle at the ageing under the action of external stresses from 50 to 150 MPa by the transmission electron microscopy (TEM) method were carried out [4,5]. The long-range internal stress fields $\langle\sigma_G\rangle$ in the aged under stress single crystals are created by combining of local stress fields from oriented formation of coherent and semicoherent Ti_3Ni_4 particles. Such long-range internal stress fields result in the oriented growth of R - and B19'-martensite during stress-free cooling of TiNi crystals and, accordingly, in the manifestation of two-way shape memory effect [1, 5].

It was previously shown [6] that in the aged at 673 K for 1 h under compressive/tensile stresses single crystals of $Ti_{49.2}Ni_{50.8}$ alloy the internal stress field $\langle\sigma_G\rangle$ depending on their orientation relative to the external stress determines the value of stress hysteresis $\Delta\sigma$, contributes to the increase in the temperature range of the superelasticity and leads to the appearance of elastic twinning of R-phase with the reversible strain up to ε_{rev}~1.4 % [6]. However, systematic studies of the effects of the number of crystallographic variants of Ti_3Ni_4 particles with different size and volume fraction on the thermoelastic martensitic transformations, mechanism of the shape memory effect and superelasticity in TiNi single crystals have not yet been carried out.

Thus, the objective of the present work is to study the dependence of the stress-induced thermoelastic B2-R-B19' martensitic transformations, superelasticity on the number of crystallographic variants of Ti_3Ni_4 particles in the $[\bar{1}11]$-oriented $Ti_{49.2}Ni_{50.8}$ single crystals aged at 823 K for 1 h in free-stress state and under a compressive stress of 150 MPa. Such researches are attractive to further development of the theory of thermoelastic martensitic transformations in structural non-uniform materials, as well as to practical use for selection of a structural state at elaboration of the TiNi shape memory alloys with specified properties.

2. Materials and methods

Single crystals from ingots of TiNi with a nominal composition of $Ti_{49.2}Ni_{50.8}$ (in at. %) were grown using the Bridgman technique in an inert gas atmosphere. From the large single crystals, dog-bone shaped samples with 16 mm gauge length and a 6 mm x 3 mm cross section were electro-discharge machined with the loading direction oriented along $[\bar{1}11]_{B2}$ in austenite. The sample orientation was verified with a DRON-3 X-ray diffractometer.

Before tests, the specimens were annealed at 1273 K for 1 h and quenched in water. Aging at 823 K, 1 h under compression stress $|\sigma|$=150 MPa is carried out in vacuum and stress-free aged samples were used as a reference condition. Stress to a sample was put after heating in a free condition up to 473 K and sample was unstressed after its cooling to 473 K to avoid stress-induced martensitic transformation during aging. After the aging process was completed, tensile specimens with 16 mm gauge length and 1.5 mm x 3 mm cross section were cut.

The microstructures were examined with a Philips CM 12 transmission electron microscope (TEM) operated at a nominal accelerating voltage of 120 kV.

The isothermal loading/unloading test was performed in an Instron 5969 universal testing machine, the strain rate was 1×10^{-3} $1 \cdot s^{-1}$. Isostress thermal-cycling tests were carried out using a miniature load frame capable of +/- 0.1 kN. The heating/cooling from 77K to 373 K was achieved by flow of cold nitrogen through a contact heating-cooling system, the heating/cooling rate was 10 $K \cdot min^{-1}$. For all cycles, stresses were first applied after an initial heating to well above A_f.

3. Results and discussion

The TEM bright field image shows that four crystallographic variants of Ti_3Ni_4 particles of 350(±30) nm in size are formed in stress-free aged crystals (figure 1(a)). In contrast, in stress-assisted aged $[\bar{1}11]$-oriented $Ti_{49.2}Ni_{50.8}$ single crystals only one variant of Ti_3Ni_4 particles with the normal to the particle habit plane parallel to the $[\bar{1}11]$ compressive axis are precipitated (figure 1(b)).

The research results of the effects of the number of particle crystallographic variants on the stress-induced thermoelastic B2-R-B19' martensitic transformation and superelasticity are presented on figures 2-4. It was experimentally established that the characteristic temperatures of martensitic transformation (M_s and M_f are the start and finish temperatures of the forward R-B19' transformation during cooling, A_s and A_f are the start and finish temperatures of the reverse B19'-B2 transformation upon heating) and the critical stresses of the stress-induced martensitic transformation are determined by the number of crystallographic variants of the disperse Ti_3Ni_4 particles.

The stress-strain responses σ(ε) of stress-assisted aged crystals with one particle variant demonstrate two critical stresses (figure 2). The first critical stress σ_{cr1} is observed within temperature range from M_s up to T_R (T_R ~ 325 K is the start temperature of the B2-R martensitic transformation during cooling) and it is associated with the reorientation of R-martensite crystals under applied stress.

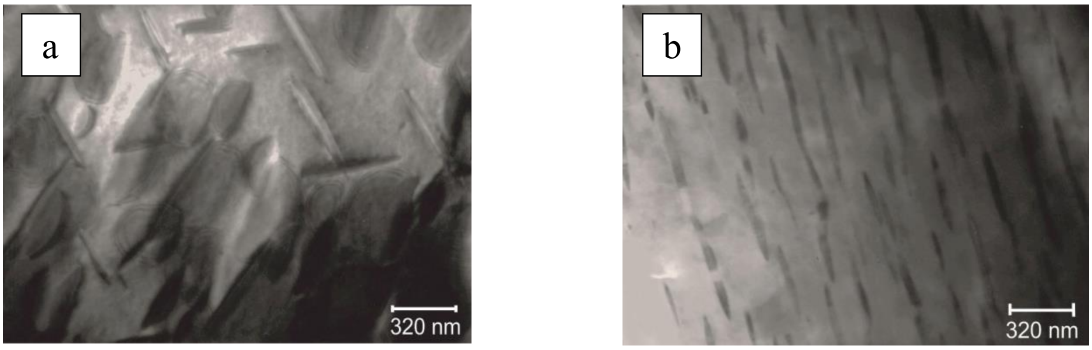

Figure 1. Microstructure of a $Ti_{49.2}Ni_{50.8}$ single crystal aged at 823 K for 1 h in stress-free state (a) and under compression stress of 150 MPa along $[\bar{1}11]$ direction (b).

The critical stress σ_{cr1} weakly decreases with increase in the test temperature. In the investigated stress-assisted aged at 823 K crystals the given strain about 0.5% arising from the reorientation of the R-phase at the applied stress $\sigma < \sigma_{cr2}$ is irreversible after unloading in contrast to aged at 673 K under compressive stress $Ti_{49.2}$N $i_{50.8}$ crystals with one variant of the particle of 30-40 nm in size [6]

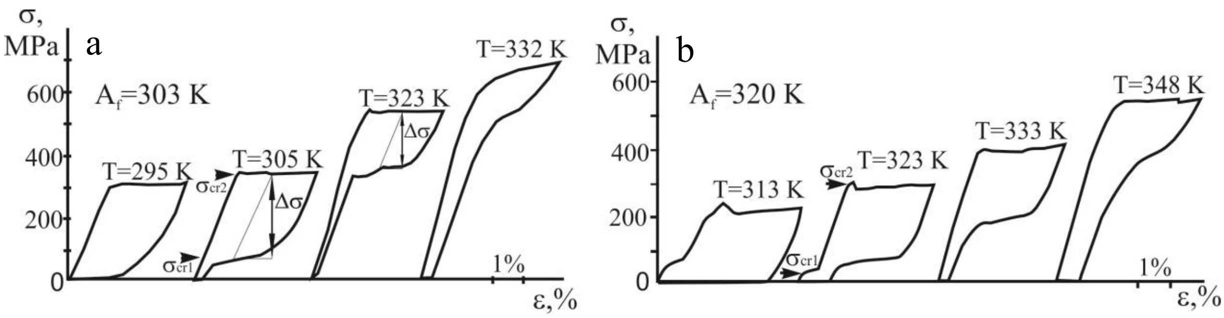

Figure 2. Stress-strain responses in tension of $[\bar{1}11]$-oriented $Ti_{49.2}Ni_{50.8}$ single crystals aged at 823 K for 1 h in stress-free state (a) and under compression stress of 150 MPa (b).

In stress-free aged at 823 K crystals the first critical stress σ_{cr1} within the temperature range $M_s<T<T_R$ is not clearly evident (figure 2) that was also observed for stress-free aged at 673 K single crystals [6]. The second critical stress σ_{cr}^2 is associated with stress-induced R-B19' martensitic transformation and it linearly increases at $T>M_s$ with the growth of the test temperature in accordance with the Clausius-Clapeyron relationship [1]

$$\frac{d\sigma}{dT} = -\frac{\Delta S^{A-M}}{\varepsilon_{tr}^{A-M}}, \qquad (1)$$

where $\Delta S^{A\text{-}M} < 0$ is the change of entropy associated with the forward transformation, ε_{tr} is the transformation strain.

Figure 3 shows the temperature dependences of the second critical stress $\sigma_{cr2}(T)$ in stress-free and stress-assisted aged at 823 K for 1 h $Ti_{49.2}Ni_{50.8}$ single crystals. These $\sigma_{cr2}(T)$-dependence can be divided into three temperature ranges, which are characteristic for alloys with a thermoelastic martensitic transformation. In the first range at $T \leq M_s$, the stress σ_{cr2} equals the critical stress for reorientation and detwinning of the B19′ martensite crystals. The aged under stress crystals have the lower level of the critical stress σ_{cr2} for reorientation and detwinning of martensite crystals in this temperature range as compared to the stress-free aged crystals (figure 3). The minimum values of σ_{cr2} are observed at $T = M_s$. In the second range $M_s < T < M_d$, the initial crystal structure is the B2-phase, and the onset of deformation is associated with the stress-induced martensitic transformation to B19′-martensite.The critical stress σ_{cr2} linear increases up to the M_d temperature. Experimentally the M_d point is defined as the temperature at which the maximum in the $\sigma_{cr2}(T)$-dependence is observed. At this point the critical stresses for formation of stress-induced martensite and for plastic flow of austenite are equal to each other. The third range $T > M_d$ is associated with the plastic flow of the B2-phase.

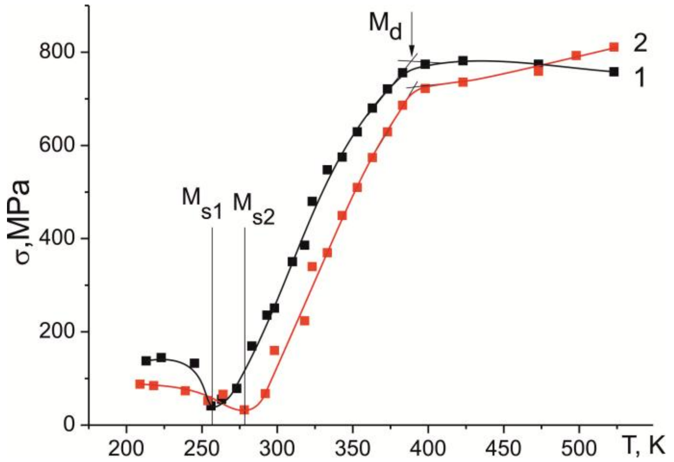

Figure 3. Temperature dependence of the critical stress level σ_{cr2} of the $[\bar{1}11]$-oriented $Ti_{49.2}Ni_{50.8}$ single crystals in tension: for aged at 823 K for 1 h crystals in stress-free state (curve 1) and under compression stress of 150 MPa (curve 2).

Figure 3 shows that for stress-assisted aged crystal the start temperature of R-B19' transformation M_{S2} is higher by 18 K than temperature M_{S1} for stress-free aged crystals with four particle variants. Such increase in the start transformation temperature M_{S2} in stress-assisted aged crystal caused by the action of the internal long-range stress field $<\sigma_G>$ which is created by combining of local stress fields from one variant of particles. In the stress-free aged crystals the long-range stress field is missing because the local stress fields from the neighboring particle variants compensate for each other. The Clausius-Clapeyron equation (1) provides to estimate the long-range internal stress field in the stress-assisted aged crystals [7]:

$$|<\Delta\sigma_G>| = \frac{\Delta S}{\varepsilon_0}\Delta M_s. \quad (2)$$

Using the experimental values of $\left|\frac{\Delta S}{\varepsilon_0}\right| = \frac{d\sigma}{dT} = 3.6\ MPa \cdot K^{-1}$ and equation (2) we determined that the long-range internal stress field $|<\sigma_G>|$ is equal to 65 MPa in the aged under stress $[\bar{1}11]$-oriented $Ti_{49.2}Ni_{50.8}$ single crystals. This internal stress field $|<\sigma_G>|$ is conducive to start of martensitic transformation at higher temperatures $\Delta M_s \approx 18$ K as compared to $[\bar{1}11]$-oriented stress-free aged crystals.

In the temperature range of stress-induced martensitic transformation ($A_f < T < M_d$) the $[\bar{1}11]$-oriented single crystals aged at 823 K for 1 h in stress-free and stress-assisted states demonstrate the superelasticity. The temperature range of the superelasticity ΔT_{SE} is defined as a temperature range in which the given strain by stress-induced martensitic transformation is complete reversibility at unloading. Regardless of the number of crystallographic variants of the disperse Ti_3Ni_4 particles ΔT_{SE}=30 K in $[\bar{1}11]$-oriented aged $Ti_{49.2}Ni_{50.8}$ single crystals. However, in crystals with one variant of particles the temperature interval of superelasticity ΔT_{SE} is shifted towards to higher temperatures due to increase in A_f as compared to stress-free aged crystals with four particle variants (figure 2).

The stress hysteresis $\Delta\sigma$ which was determined as the stress difference between the forward and the reverse stress-induced transformation at the middle of the superelasticity curve characterizes the dissipation energy at stress-induced martensitic transformation. A reduction of the stress hysteresis $\Delta\sigma$ with increase in test temperature is observed in investigated crystals. A similar reduction in $\Delta\sigma(T)$ by a factor of 3-8 is reported for TiNi (C_{Ni} > 50.6 at.%) single crystals that contained Ti_3Ni_4 particles with sizes of d < 40 nm [3].

Figure 4 shows the strain-temperature responses ε(T) recorded during cooling/heating under constant tensile stress of 0.7, 10 and 100 MPa for the stress-free and stress-assisted aged crystals. Stress-assisted aging of the $[\bar{1}11]$-oriented single crystals resultes in appearance of two-way shape memory effect as it is shown in figure 4(b). Upon cooling stress-assisted aging crystal spontaneously expands in the $[\bar{1}11]$-direction at near zero stress. It should be noted that a minimum tensile stress of σ < 1 MPa was required to securely clamp the samples in the setup. Upon heating, the sample dimensions are completely restored and the reversible two-way shape memory effect strain ε_{TWSME} = +2.3(±0.3)% is observed (figure 4(b)). The internal stress field of $|\langle\sigma_G\rangle| \approx 65$ MPa from the oriented growth of dispersed particles in the stress-assisted aged crystals promotes the oriented growth of martensite in cooling, which in turn gives rise to the two-way shape memory effect.

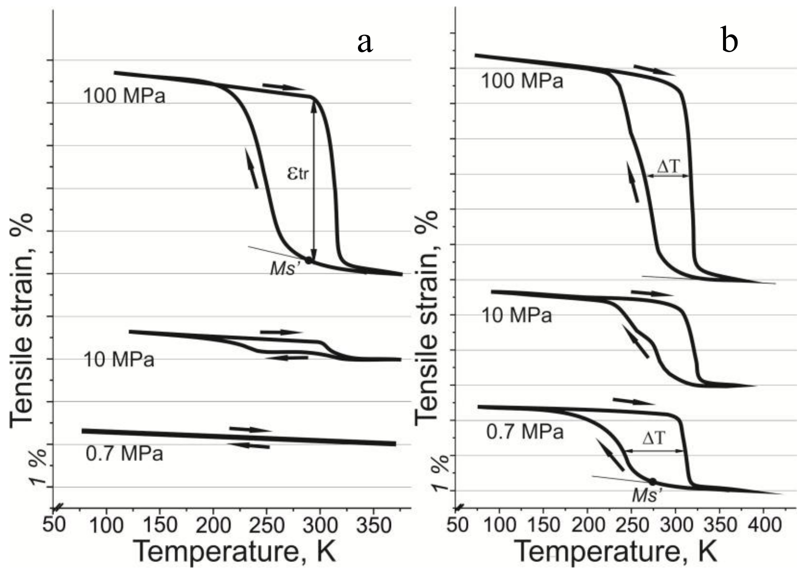

Figure 4. Strain-temperature ε(T) responses of $[\bar{1}11]$-oriented $Ti_{49.2}Ni_{50.8}$ single crystals during cooling/heating under constant tensile stress: for aged at 823 K for 1 h crystals in stress-free state (a) and under compression stress of 150 MPa (b).

In contrast, the stress-free aged crystals do not demonstrate the two-way shape memory effect (figure 4(a)). So, in these crystals during the cooling process a self-accommodated microstructure of martensite is formed in the stress range from 0 to 8 MPa. Under larger tensile stresses the oriented martensite is formed, its volume fraction and the reversible transformation strain increase with stress magnitude.

The martensite start temperature (M_s') increases linearly with the stress value according by Clausius-Clapeyron relationship (1) for both aged crystals. As marked for the ε(T)-respons in figure 4 transformation strains ε_{tr} and thermal hysteresis ΔT were defined as the vertical and horizontal width of the loops, respectively. A decrease in the thermal hysteresis ΔT and growth in ε_{tr} are observed for both crystal, the value of the ε_{tr} at cooling-heating cycle at tensile stress of 100 MPa is, however, larger in the crystals aged under stress (figure 4).

4. Summary

In this study the effects of stress-free and stress-assisted aging at 823 K for 1h on the stress-induced B2-R-B19′ martensitic transformation and superelasticity in $Ti_{49.2}Ni_{50.8}$ (at. %) single crystals are established. It is experimentally shown that aging in a free condition results in precipitation of four variants of Ti_3Ni_4 particles of 350(±30) nm in size oriented along four cristallographically equivalent $\{111\}_{B2}$ planes. Thus, the local stress fields from the neighboring particle variant compensate for each other in stress-free aged crystals. Upon aging under compression stress of 150 MPa along $[\bar{1}11]$ direction only one variant of Ti_3Ni_4 particles grows. The precipitation of one variant of Ti_3Ni_4 particles in the stress-assisted aged $Ti_{49.2}Ni_{50.8}$ single crystals leads to appearance of homogeneous long-range internal stress field $|\langle\sigma_G\rangle| \approx 65$ MPa, which is created by combining of local stress fields from one variant of particles. The existence of internal long-range stress field in $Ti_{49.2}Ni_{50.8}$ single crystals aged under stress results in, firstly, the increase in the characteristic temperatures of martensitic transformation similar to the effect of external stresses according to the Clausius-Clapeyron equation (1). Secondly, during stress-free cooling in the crystals with one variant of particles R-martensite is formed in accordance with the internal stress field and it is reoriented when an external tensile stress reaches to critical stress level of σ_{cr1} within the temperature range from M_s up to T_R. Thirdly, the growth oriented martensite during stress-free cooling the stress-assisted single crystals with one variant of Ti_3Ni_4 particles is confirmed by observation of the two-way shape memory effect. The sample during stress-free cooling spontaneously undergoes strain of 2.3%, which is fully reversible by heating.

Acknowledgments

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