Martensitic Transformations in TiNi Alloys with Ti₃Ni₄ Precipitates

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Abstract. The thermoelastic martensitic transformations in Ti₄₀Ni₅₀ and Ti₄₈Ni₄₂ alloys after isothermal aging have been studied by means of transmission electron microscopy and dilatometry. The presence of Ti₃Ni₄ precipitates and the difference in precipitates size affect the martensite nucleation and martensitic transformation temperatures and sequences in TiNi alloys. Highly coherent and densely dispersed Ti₃Ni₄ particles (<20-50 nm length) after initial aging stages depresses B₂→B₁₉’ transition and initiates B₂→R one. The Ti₃Ni₄ particles provide the nucleation sites for the R-martensite. When size of Ti₃Ni₄ particles run from 100 nm to 1–2 μm, decreasing of number of Ti₃Ni₄ variants and thus R-phase ones is observed. Transformation sequence is B₂→R→B₁₉’. When sizes of Ti₃Ni₄ particles run as large as several microns, they provide nucleation sites of the B₁₉’-martensite. Transformation sequence is B₂→B₁₉’ as in solution treated specimen.

1. INTRODUCTION

The Ti₃Ni₄ particles, precipitating in TiNi alloys rich in nickel, exert considerable influence on characteristics of martensitic transformations [1-3]. This is caused by the fact that the process of Ti₃Ni₄ precipitation has several stages [4] and by the possibility of obtaining different types of bimodal size distribution of particles [5]. Size distribution as well as changes in size of the Ti₃Ni₄-precipitates are important factors that affect martensitic transformations and thus the shape memory effect in TiNi alloys. This paper presents the results of research of Ti₃Ni₄ particle sizes’ influence on characteristics of the subsequent martensitic transformations. Observations of R- and B₁₉’- martensite nucleation in aged TiNi specimens are also presented in this work.

2. EXPERIMENTAL PROCEDURE

Alloys with a high nickel content, which correspond to Ti₄₀Ni₅₀ and Ti₄₈Ni₄₂, were prepared by melting in an arc furnace with a water-cooled copper base. To ensure homogeneity, the ingots were remelted at least three times. subsequently they were hot rolled in several passes to 2-mm-thick plates with a intermediate heating to 850 °C. The as-rolled plates were heated to 870 °C, held for 0.5 h, and quenched at the rate of 600°C/min. Then the plates were subjected to isothermal aging at a temperatures 250–550 °C. The plates were cut into specimens oriented by their long sides along the rolling direction for dilatometry and electron microscopy. Thin foils were prepared by abrasive grinding and subsequent electropolishing in an electrolyte of 10 % HClO₄ and acetic acid at U = 20 V and T = +5 °C. The structure was examined using a JEM-200CX electron microscope at 200 kV. Dilatometric measurements were carried out using a Chevenard dilatometer equipped with a furnace and a cryostat.

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3. RESULTS and DISCUSSION

B2→B19' martensitic transformation takes place in TiNi alloys with high nickel content in solution-treated state. The dilatometric curve of the Ti<sub>40</sub>Ni<sub>51</sub> solution-treated specimen is shown on fig.1a. A large

![Graph showing dilatometric curves of martensitic transformations for Ti<sub>40</sub>Ni<sub>51</sub> alloy.](image)

Figure 1: Dilatometric curves of martensitic transformations for Ti<sub>40</sub>Ni<sub>51</sub> alloy. (a) After solution treatment, solution treated followed by aging at (b) 250 °C 30 min. (c) 350 °C 30 min. (d) 350 °C 30 min (Ti<sub>40</sub>Ni<sub>51</sub>). (e) 425 °C 5 min. (f) 425 °C 5h. (g) 500 °C 2h and (h) slow cooling from 870 °C to 20 °C (rate 0.6 °C/min)
temperature histeresis about 30 degrees corresponds to $\text{B}2\leftrightarrow\text{B}19'$ transformation. The $\text{B}2\rightarrow\text{B}19$ transition during cooling is accompanied by length increase.

Upon aging at 250 °C disperse particles rich in nickel [4] precipitates, which sizes are about several nanometers. There is a possibility that chemical composition of these particles differs from the Ti$_3$Ni$_4$ by lesser nickel content [5]. The dilatometric curve for the specimen aged at 250 °C for 30 min allows to consider that the sequence of martensitic transformations in the alloy is $\text{B}2\leftrightarrow\text{R}$ (temperature histeresis is several degrees). B19'-martensite formation is not noticed until -196 °C (fig.1b). The $\text{B}2\rightarrow\text{R}$ transformation is accompanied by increase of the samples' length.

The curve, i.e. transformation behavior, for the specimen aged at 350 °C is essentially the same as that for the specimen aged at 250 °C. Raising the aging temperature to 350 °C results in the $\text{B}2\rightarrow\text{R}$ transition temperature ($T_R$) increase, the $\text{B}2\langle\text{R}\rangle\rightarrow\text{B}19'$ transformation still doesn't take place (fig.1c). After such treatment disperse particles of sizes not exceeding 10 nm can be found in the alloy's structure. Stress fields around the particles rise as the particles grow larger. This circumstance can explain the increase of $T_R$ temperature [1]. Fig.2 shows an R-martensite structure in Ti$_{40}$Ni$_{51}$ aged at 350 °C for 5 h. Two groups of parallel plates illustrate one of the R-martensite crystal grouping types. Disperse particles of Ti$_3$Ni$_4$ are present inside all the plates of R-martensite.

![Figure 2: Electron micrograph of R-phase in the Ti-51 at.%Ni alloy aged at 350 °C for 5 h](image)

With further aging temperature raises two martensitic transformations ($\text{B}2\rightarrow\text{R}\rightarrow\text{B}19'$) take place in the alloy during cooling. Their temperature intervals are separate, and both transformations take place with length increase (fig.1d,e).

Upon cooling in the TEM observations of an alloy aged at 425 °C for 5 min show the nucleation of R-martensite crystals on Ti$_3$Ni$_4$ particles. Fig. 3 shows that the particles formed in B2-matrix are inherited by R-martensite, and hence the boundaries of R-martensite plates are not rectilinear. B19'-martensite also inherits the disperse Ti$_3$Ni$_4$ particles, which can be clearly seen by uneven sinuous edges of the growing B19' plates (fig.4). The observation during cooling in the TEM of an alloy aged under 425 °C for 30 min shows that B19' crystals grow independently of R crystals. This is indicated by their interposition as well as R crystals displacement when intersected by B19' (fig.4).

It is remarkable that Ti$_3$Ni$_4$ particles lining trend can be observed in Ti$_{40}$Ni$_{51}$ aged at 350 °C for 5 h. Progressive enhancement of lining (orientations selection) can be observed with increasing in temperature and aging duration, when the particle sizes grow as large as 20 to 100 nm (fig.5). One orientation becomes clearly preferable when the particle sizes reach 100 nm to 1 μm. The darkfield observations show that there are regions dominated by particles of one orientation.
Ordered arrangement of particles is essential for characteristics of $B_2 \rightarrow R$ transformation. That's why we introduce here the term ‘first critical size’ of $Ti_3Ni_4$ particles, which corresponds to the beginning of the lining process. After aging of $Ti_{49}Ni_{51}$ alloy at 350 °C for 10 h and 425 °C for 5 min when lining begins, a change of the dilatometric curve takes place (fig.1e): during $B_2 \rightarrow R$ transformation the curve lowers first, and then rises, i. e. first the sample shortens a little and then expands. With increase in duration of aging under 425 °C and also after aging under 500 °C this process goes further: $B_2 \rightarrow R$ transformation takes place with decrease of the samples’ length (fig.1f). Martensitic transformations sequence after such treatments is $B_2 \leftrightarrow R \leftrightarrow B_{19'}$. The total linear effect is close to zero with aging under 425 °C for 2 h and 500 °C for 30 min. The sizes of $Ti_3Ni_4$ particles are about 50 and 100 nm respectively. With increase in duration of aging under 500 °C to 2-5 h the form of the dilatometric curve shows that $B_2 \rightarrow R \rightarrow B_{19'}$ martensitic transformations take place during cooling, and $B_{19'} \rightarrow B_2$ transformation —
during heating (fig.1g). It is possible that temperature intervals of $B19' \rightarrow R$ and $R \rightarrow B2$ transitions overlap. Total dilatometric effect during cooling changes the sign.

The forms of dilatometric curves on fig.1 shows that aging of TiNi alloys under different temperatures and duration times allows to vary the temperatures and temperature intervals of martensitic transformations within the wide range. Note that basic regularities of temperature changes of martensitic transformations and their sequence established for Ti$_{40}$Ni$_{51}$ are not different in the main from those of Ti$_{48}$Ni$_{52}$. At the same time some peculiarities of martensitic transformations behavior in the Ti$_{48}$Ni$_{52}$ alloy found, conditioned by the higher nickel content in matrix, i.e. the higher extent of supersaturation by nickel.

From the comparison of dilatometric measurements and electron microscopy observations follows that these disperse Ti$_3$Ni$_4$ particles and middle size particles (approx. 1µm) coherent with B2-matrix exerts initiating influence on the matrix towards B2→R transition. First and foremost, epitaxial growth of R-martensite on the Ti$_3$Ni$_4$ particles is possible because of similarity of crystal lattices: planes (111) of lattices of both phases are parallel. Rombohedral distortions in B2-matrix caused by coherent Ti$_3$Ni$_4$ particles also contribute to the B2→R transformation. The dilatometric effects sign change during the B2→R transformation can be explained by the following. Lining of particles within one B2-phase crystallite, provided the original B2-matrix has texture [7], results in orientation of stress fields over the whole sample. Hence the selection of R-martensite orientations takes place, i.e. of all crystallographically equivalent orientations only distinct (preferable) orientations of R-martensite are selected during the B2→R transformation.

When the particle sizes reach 1 µm, obvious cases of R-martensite nucleation on Ti$_3$Ni$_4$ particles are discovered. In fig.6 we observed nucleation of R-martensite on coarse particles. The diffraction contrast at the edges of R-martensite plates and at the edges of Widmanstatten particles of Ti$_3$Ni$_4$ provides evidence of coherency of all three phases: B2, R and Ti$_3$Ni$_4$. Fig.6 shows that R-martensite crystals grow by steps.

As described in [5, 6], large Ti$_3$Ni$_4$ particles (up to 10 µm) can be obtained resulting from slow cooling of alloys from single phase B2-area. As Ti$_3$Ni$_4$ particles grow coarser, the coherency between

![Figure 6: R-martensite nucleation on the Ti$_3$Ni$_4$ particles in Ti$_{48}$Ni$_{52}$ aged at 550 ºC for 10 h](image)

![Figure 7: B19'-martensite nucleation around Ti$_3$Ni$_4$ particles in Ti$_{48}$Ni$_{52}$ Slow cooling from 870 C to 400 C (rate 0.6 ºC/min ) then water cooling](image)
particles and matrix disappears. The formation of dislocations points towards relaxation of the coherency stresses. Here we introduce the term ‘second critical size’ of Ti$_3$Ni$_4$ particles which corresponds to the loss of coherency between matrix and particles. The particles in this state do not serve as nucleation sites of R-martensite. Lesser nickel content of the matrix and its shift towards equiatomic composition results in rise of B2$\rightarrow$B19' transformation start temperature. The particles are covered by twinned B19'-martensite coating (fig.7). The inner structure of B19'-martensite crystals is twins of the same orientation on both sides of the particle. The crystals themselves are oriented along the particle. B19' crystals’ growth is limited by nickel content of the matrix. The decisive factor here is depletion of the matrix from nickel, resulting in increase of the B2$\rightarrow$B19' transformation temperature. After cooling of the Ti$_{48}$Ni$_{52}$ alloy with cooling rate of 1.5-3 °C/min [5] and the Ti$_{49}$Ni$_{51}$ — with 1.0 or 0.6 °C/min rates, the particle sizes are as large as several micrometers (up to 10μm) [6]. The transformation sequence in these cases is B2$\rightarrow$B19' (fig.1h). Compared to solution treated state, when the B2$\rightarrow$B19' transformation is observed (fig.1a), the Ms temperature is significantly higher. Another peculiarity is the wide temperature interval of the martensitic transformation (80-100 °C).

Thus, we see that the second critical size of Ti$_3$Ni$_4$ particles (approx. 1μm), introduced above, is a limit, below which the particles serve as nucleation sites of R-martensite, and the particles above the second critical size promote B19'-martensite formation. This critical size is defined by the extent of coherency between the matrix and the Ti$_3$Ni$_4$ particles.

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References