



Article Structure and Multistage Martensite Transformation in Nanocrystalline Ti-50.9Ni Alloy

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Abstract: An electron microscopic study of the evolution of the size, morphology, and spatial distribution of coherent Ti_3Ni_4 particles with a change in the aging temperature in a nanocrystalline (NC) Ti-50.9 at % Ni alloy with an inhomogeneous grain–subgrain B2-austenitic nanostructure has been carried out. It was found that with an increase in the aging temperature, along with a change in the size and shape of Ti_3Ni_4 nanoparticles, their spatial distribution changes from location at dislocations to precipitates at subboundaries. Research has shown that the presence of different types of internal interfaces in the nanostructure contributes to the heterogeneous distribution of coherent Ti_3Ni_4 nanoparticles in the volume of the B2 matrix, which is associated with the precipitation of particles in the region of low-angle subboundaries and the suppression of the Ti_3Ni_4 precipitation in nanograins with high-angle boundaries. The difference in the structural-phase state of nanograins and subgrains regions is the main reason for the implementation of the anomalous R-phase transformation effect in the sequence of multistage martensitic transformations B2 \leftrightarrow R \leftrightarrow B19'.

Keywords: nanocrystalline TiNi alloy; annealing; grain–subgrain structure; Ti_3Ni_4 particles; martensite transformations

1. Introduction

Nanocrystalline TiNi alloys with unique properties of shape memory effect and superelasticity, due to the reversible transformation between B2-austenite and B19' martensite, have high strength and functional stability and are widely used in medicine [1,2]. Their representatives in biomedicine are Ni-rich TiNi alloys, which are aged with the formation of coherent Ti_3Ni_4 particles [1–3]. Such precipitates in TiNi polycrystals can change the path of martensitic transformations from $B2 \rightarrow B19'$ to the sequence of transformations through the transition R-phase: $B2 \rightarrow R \rightarrow B19'$ [3–5]. This is mainly due to inhomogeneous Ti₃Ni₄ particles distribution in B2-austenite grains and the associated difference in the Ni content between B2-austenite grain volumes and boundaries [6,7]. However, in NC TiNi alloys with a large volume fraction of interfaces, the cause of multistage transformations is unclear, and the formation of coherent Ti₃Ni₄ particles as well as their spatial distribution is poorly understood. This is largely due to the lack of data on the localization of coherent Ti₃Ni₄ particles in the nanostructure of TiNi alloys due to the complexity of their detection and certification in NC material. In addition, the study of NC TiNi alloys is complicated by the necessity of accounting for grain refinement and associated increase in critical martensite shear stresses [8], possible suppression of B2-austenite solid solution decomposition in nanograins [9], and high defect density in the nanostructure after severe deformation [10]. Another important factor is that the nanostructure of TiNi alloys after cold deformation is highly inhomogeneous. For example, a mixed grain–subgrain B2 structure is typical of textured TiNi after severe cold deformation [11]. Such a structure is observed in semifinished products (wires, thin-walled tubes, etc.) used for manufacturing various medical



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). devices. The purpose of this work is to better understand the effect of the size and spatial distribution of Ti_3Ni_4 particles in grain–subgrain nanostructure of an aged Ti-50.9 at % Ni alloy on the multistage character of martensite transformations. This knowledge can be used to fine-tune the interval of martensitic transformations in NC Ni-rich TiNi alloy tubing in the process of medical implants manufacturing.

2. Materials and Methods

The test material was a commercial nanocrystalline TiNi alloy with a Ni content of 50.9 at % (Vascotube GmbH, Birkenfeld, Germany). The tubular samples cut from microtubes for medical stents were annealed at 300 °C (low-temperature aging) and 400 °C (region of the highest rate of Ti₃Ni₄ precipitation) for 1 h with further water quenching at room temperature. These aging treatments will allow the precipitation of Ti₃Ni₄ particles differing in size and morphology. The start and finish temperatures of direct and reverse B2 \leftrightarrow R \leftrightarrow B19' transformations were determined by electrical resistivity measurements. In all specimens, the sequence of direct and reverse martensite transformations was B2 \leftrightarrow R \leftrightarrow B19'. The critical start temperatures of B2 \rightarrow R (T_R) as well as the start and finish temperatures of R \leftrightarrow B19' (M_S, M_F, A_S, A_F) determined by resistivity measurements are presented in Table 1. The features of B2 \leftrightarrow R \leftrightarrow B19' transformations were analyzed on a NETZSCH DSC 404 F1 differential scanning calorimeter with a heating and cooling rate of 10 K/min.

 Table 1. Martensite transformation temperatures in nanocrystallineTi-50.9Ni alloy.

Temperature	T _R , °C	Μ _S , °C	M _F , [◦] C	A _S , [◦] C	A _F ,°C
Initial	7	-74	-140	-45	-26
300 °C	22	-50	-130	-37	-14
400 °C	33	-30	-115	-2	15

The structure of the specimens cut along the microtube axis was studied on a JEOL JEM 2100 transmission electron microscope. The preparation of thin foils included grinding, mechanical polishing to a thickness of 0.1 mm, and ion thinning on a JEOL EM 09100IS ion slicer. The average size of grains and subgrains was determined by measuring the average diameter of no less 100 grains on bright- and dark-field images. A comparative analysis of the size of the Ti₃Ni₄ precipitations in samples heat-treated at various temperatures was carried out mainly on dark-field images.

3. Results

3.1. Microstructure Characterization

The initial alloy has an inhomogeneous hierarchical B2-austenite nanostructure with elements of two scales: conglomerates of slightly misoriented nanosubgrains of micron sizes and nanograins with high-angle boundaries, which provides a wide range of internal interfaces (Figure 1). There are two types of nanograins: (i) dislocation-containing nanograins formed under severe deformation and further annealing and (ii) dislocation-free nanograins crystallized from amorphous state [11]. The average size of dislocation-free nanograins with high-angle boundaries is 70 nm. In subgrains of size 40–60 nm, a high dislocation density is observed. Such subgrains, having imperfect low-angle boundaries azimuthally misoriented by less than 3° , form regions of up to 800 nm (Figure 1b). On selected area electron diffraction (SAED) patterns, the grain–subgrain structure is represented mostly by circular point reflections. In addition to B2-austenite reflections, there are individual reflections identifiable as R-phase and Ti₃Ni₄-phase reflections.



Figure 1. Bright-field image of mixed grain–subgrain structure with a submicron subgrain region, corresponding SAED pattern from the circled region, zone axis [331] (**a**), and dark-field image (**b**) in B2-austenite reflection ($1\overline{10}$).

Figure 2 shows the structure of the alloy after annealing at 300 °C. Such low-temperature aging involves recovery and polygonization processes, dislocation density reduction, and dislocation rectification of low-angle boundaries, but the size of grains and subgrains remains, on average, unchanged. In the structure, coherent Ti₃Ni₄ particles smaller than 10 nm precipitate (Figure 2a,b), which is characteristic of the initial stage of B2 phase decomposition in TiNi during low-temperature aging [12]. Such particles precipitate mostly inside subgrains and at dislocations, showing weak reflections in positions 1/7 along the B2 lattice directions <321> (Figure 2c) and a "coffee bone" contrast induced by elastic distortion fields (Figure 2b). For comparison, dislocation-free grains are shown (Figure 2e,f), which are usually several tens of nanometers in size. No dislocations were found in these nanograins at admissible tilt angles. In addition, such grains did not show a clear TEM diffraction of Ti₃Ni₄ precipitates. Figure 2c shows that on the SAED patterns, the diffraction spots occurring at 1/3 < 110 > B2 are observed, indicating the formation of an R-phase. This is consistent with the data in Table 1, which show that the B2- and R-phases coexist at room temperature. As can be seen on the dark-field image in a (102)reflex (Figure 2d), disperse and imperfect morphology of R-martensite is observed.



(a)

(b)

Figure 2. Cont.



Figure 2. Structure of Ti-50.9Ni after annealing at 300 °C: (**a**) bright-field image of subgrains and corresponding SAED pattern, arcs correspond to the positions of reflections of B2, (**b**) bright-field image of large grain with "coffee bone" contrast indicative of the presence of coherent Ti₃Ni₄ particles, (**c**) corresponding SAED pattern showing weak reflections of Ti₃Ni₄ particles in positions 1/7 along the B2 lattice directions <321> (dark arrows), zone axis [135], the R-phase reciprocal lattice section is indicated by white lines, (**d**) R-phase dark-field image in a ($\overline{102}$) reflection indicated by white arrows on (**c**), (**e**,**f**) bright-field image of dislocation-free grains and corresponding dark-field in (011) reflection of B2 on SAED pattern.

The precipitation of Ti₃Ni₄ particles at dislocations during low-temperature annealing is due to the low volumetric diffusion of atoms and the predominance of diffusion of atoms along dislocation tubes. It should be noted that this type of precipitate is found in dislocation-containing nanograins and is not found in dislocation-free nanograins. Such Ti₃Ni₄ nanoparticles are rarely observed in grain boundary–subboundary regions because the low aging temperature (300 °C) does not allow Ni atoms to diffuse from internal grain–subgrain volumes to their boundaries. The fine Ti₃Ni₄ particles decorate the few dislocations present in nanograins. Our results agree with data on polycrystalline TiNi alloys whose structure after low-temperature annealing (<330 °C) contains a large amount of coherent spherical nanoparticles of diameter <10 nm [12,13].

Annealing at 400 °C decreases the dislocation density and slightly widens the size range of polygonized nanograins, i.e., no recrystallization occurs. At the stage of recovery, dislocations inside subgrains are redistributed such that some of them are annihilated and others escape to low-angle subboundaries. As a result, the subboundaries change

their shape from linear after annealing at 300 °C (Figure 2a,b) to convex after annealing at 400 °C (Figure 3). Their bright-field images reveal a diffuse diffraction contrast (Figure 3) which can be indicative of their nonequilibrium state [14,15] due to substantial B2 matrix distortion in elastic stress fields induced by excess dislocations and by coherent Ti₃Ni₄ particles formed at subgrain boundaries [15].



(a)



(c)

Figure 3. Subgrain structure of Ti-50.9Ni with Ti₃Ni₄ particles after annealing at 400 °C: (a) brightfield images with arrows for particle lines near low-angle boundaries, (b) dark field in reflection {101} of Ti₃Ni₄ particles, (c) SAED pattern, solid and dash arcs correspond to positions of reflections of R-and Ti₃Ni₄-phases.

Under annealing at 400 °C, the alloy undergoes intense aging due to intense Ti_3Ni_4 precipitation at 400–450 °C [16]. As can be seen from Figure 3c, its microdiffraction patterns reveal numerous point reflections of R martensite and Ti₃Ni₄ particles precipitated mainly in nonequilibrium subboundary regions.

The shape of Ti_3Ni_4 particles is close to lenticular with a lateral dimension of up to 5 nm and length of up to 20 nm. Their tendency to line up in rows in the planes {111} is observed. In Figure 3a, one can identify lines of Ti_3Ni_4 particles adjacent to subboundaries. Such an arrangement points to their autocatalytic character, which compensates the nucleation and growth energy of Ti_3Ni_4 [5]. The morphology of Ti_3Ni_4 particles is such that they can lose their lenticular shape caused by the lattice mismatch between Ti₃Ni₄ and B2 matrix [5]. Apparently, this is due to their asymmetric growth under the action of high inhomogeneous stress fields near subboundaries [5,17]. In our analysis, no lenticular Ti₃Ni₄ particles and lines were found in nanograins with high-angle boundaries, and this agrees with the

conclusion that in TiNi aged at 400 °C, the B2 phase decomposition with the formation of Ti_3Ni_4 particles in nanograins smaller than 150 nm is suppressed [9].

At room temperature, the alloy aged at 400 °C has a two-phase state: B2-austenite and R-phase (Table 1). Considering that the grain and subgrain sizes remain unchanged, we think that the intense formation of Ti_3Ni_4 effectively decreases the Ni concentration in the B2 matrix and increases the temperature of B2 \leftrightarrow R transformations (T_R). The R-phase is dispersed into nanodomains, and its morphology is mostly imperfect (Figure 4b), which is due to the effect of elastic stress fields created by coherent Ti_3Ni_4 particles and dislocations. This phase is present in substructural regions and is not present in nanograins free of dislocations and particles. The transformation to the R-phase can cover the whole volume of individual subgrains and their groups (Figure 4).



Figure 4. R-phase in substructure: (**a**) bright-field image with complex contrast created by Ti_3Ni_4 particles, dislocations, and R-phase; corresponding microdiffraction pattern, zone axis [112], reflections from B2-phase are indexed, R-phase reciprocal lattice section are indicated by white lines (**b**) corresponding dark-field image in R-phase reflection ($\overline{3}10$) are indicated by white arrow on (**a**) with visible phase dispersion.

3.2. Multistage Martensite Transformations

Figure 5 shows calorimetric curves for NC Ti-50.9Ni alloy in the initial state and aged at 300 °C and 400 °C. DSC peaks were interpreted using the results of measuring the temperatures of martensitic transformations by the thermoresistometry method, presented in Table 1, as well as the above results of structural studies of aged alloy samples by the TEM method. On cooling, the initial NC alloy reveals two diffuse exothermal peaks due to direct $B2 \rightarrow R$ and $B2 \rightarrow B19'$ transformations characteristic of aged TiNi alloys with defect B2 structure [18]. On heating, it shows a single broad endothermal peak corresponding to B19' \rightarrow R \rightarrow B2 transformations. The latent heats Δ H of the B2 \rightarrow R and the $R \rightarrow B19'$ transformations were 3.8 and 2 J g⁻¹, respectively. The $R \rightarrow B19'$ transformation is significantly suppressed, showing a low and broad exothermal peak. Thus, we can assume that the sample exhibited a single-stage B2 \rightarrow R transformation on cooling and a single stage R \rightarrow B2 transformation on heating. It can be seen that after aging at 300 °C, the peaks on the DSC curves represent B2 \rightarrow R and B2 \rightarrow B19' on cooling and B19' \rightarrow R and R \rightarrow B2 on heating, which are the normal two-stage martensitic transformations for aged Ti-Ni alloys. The corresponding value of $\Delta H_{A \to R}$ was 5.4 J g⁻¹ and that of $\Delta H_{R \to A}$ was 5.3 J g^{-1} . These values are in the range of 1–6 J g^{-1} for B2 \leftrightarrow R transformations [19]. The diffuse nature of these peaks does not allow a sufficient accuracy the temperature hysteresis, but the estimate gives a value of about 6 °C, which is the typical characteristic of R-phase transformation. Thus, it can be deduced that these DSC peaks represent B2 \rightarrow R and R \rightarrow B2, respectively, which is also close to the data presented in Table 1.



Figure 5. Calorimetric curves for cooling (upper traces) and heating (lower traces) of Ti-50.9Ni in initial state and annealed at 300 $^{\circ}$ C and 400 $^{\circ}$ C for 1 h.

Another form of calorimetric curves is observed for the alloy aged at 400 $^{\circ}$ C (Figure 5). On cooling, the B2 \rightarrow R transformation occurred over a broad temperature range. As can be seen from Figure 5, the narrow $B2 \rightarrow R$ peak has a shoulder on the left, which can be interpreted as at least one additional peak. The bases of the peaks merge, giving no way to separate additional peaks with sufficient accuracy. The combined latent heat of this peak is 6.8 J g⁻¹. As shown above, aging at 400 °C leads to intense Ti₃Ni₄ particles precipitation that shifts the B2 \rightarrow R transformation to higher temperatures. As a result, the R-phase is stabilized and the $R \rightarrow B19'$ is significantly suppressed, showing a very broad exothermal peak. The blurring of the exothermal peak corresponding to $R \rightarrow B19'$ is due to the particle distribution inhomogeneity and to the extended temperature range of this transformation as R_1 , $R_2 \rightarrow B19'$. The latent heat of this peak is 3.3 J g⁻¹. We cannot exclude the implementation in a number of nanograins of the direct transformation B2 \rightarrow B19'. On heating, two merging peaks corresponding to successive B19' \rightarrow R and $R \rightarrow B19'$ transformations are observed (Figure 5). Though merging, the main peaks for the direct and reverse $B2 \leftrightarrow R$ transformations on cooling and on heating are rather narrow and well identifiable, which makes it possible to determine the temperature hysteresis as 5.6 °C. The small hysteresis confirms the correspondence of these peaks to $B2\leftrightarrow R$ transformation. The results obtained for NC Ti-50.9Ni alloy after aging under conditions of intense Ti₃Ni₄ precipitation are consistent with the Table 1 and TEM data, according to which T_R is 33 °C and the alloy is in the B2 + R state.

Thus, we can assume that the broad B2 \rightarrow R peak upon cooling contains two peaks corresponding to the B2 \rightarrow R₁ and B2 \rightarrow R₂ transformations. The TEM analysis results allow us to interpret these peaks as follows: (i) first, the transformation B2 \rightarrow R₁, which is characterized by quite high and narrow peaks developing in the substructure prevailing in the volume of the grain–subgrain nanostructure; (ii) then, there is a temperature-extended transformation of B2 \rightarrow R in groups of nanograins, which is designated as B2 \rightarrow R2.

4. Discussion

Aging at different temperatures is found to provide coherent precipitation of Ti_3Ni_4 particles differing in size, morphology, and spatial distribution in grain–subgrain structure and cause different variations to the transformation behavior of NC Ti-50.9Ni alloy. After aging at 300 °C, coherent particles precipitate mainly in the subgrain structure at dislocations. At the same time, Ti_3Ni_4 particles are not observed in dislocation-free nanograins but precipitate in nanograins, including those with a size less than 100 nm in the case of the presence of dislocations in them. Thus, the initial non-uniform grain-subgrain structure of the NC Ti-50.9Ni alloy causes an inhomogeneous distribution of both Ti_3Ni_4 precipitates and dislocations in the nanostructure. We believe that the reason for this precipitation behavior during aging at 300 °C lies in the features of the initial NC structure formation after severe cold deformation.

As noted above, two types of nanograins can be distinguished in the NC TiNi grainsubgrain structure: dislocation-containing nanograins formed under deformation and dislocation-free nanograins crystallized from amorphous state [10,11]. Unfortunately, it is impossible to determine with a sufficient degree of reliability in each case the type of observed nanograins without a special study. Reasoning from our analysis, the absence of Ti₃Ni₄ particles in dislocation-free nanograins suggests that their precipitation during low-temperature aging needs such defects as dislocations [12,13]. This conclusion agrees with data [19] showing that TiNi nanograins crystallized from an amorphous state are unfavorable for Ti₃Ni₄ precipitation in terms of the energy requirements energy due to the release of stored energy and in terms of chemical composition. In addition, the R-phase which usually nucleates at the interfaces between the particle and the matrix [2,6,20] is not detected in dislocation-free nanograins, which is consistent with the absence of coherent Ti₃Ni₄ particles in such nanograins.

It was found that with an increase in the aging temperature to 400 °C and the diffusion mobility of Ni atoms, the size of Ti_3Ni_4 nanoparticles increases, their shape changes from spherical to lenticular, and the spatial distribution in the nanostructure changes from location at dislocations to precipitation at subboundaries. No aging effects were found in nanograins. It is believed that the suppression of the deposition of coherent particles is provided by geometric constraints on the side of high-angle boundaries, which prevent the formation of arrays of self-accommodated lenticular particles inside nanocrystalline grains [5,6]. Thus, the presence of different types of internal boundaries (low-angle and high-angle) in the grain–subgrain TiNi nanostructure is the main factor affecting the process of heterogeneous nucleation of coherent Ti_3Ni_4 particles at temperatures of intense decomposition of the B2 solid solution. Such precipitates emerge in the region of low-angle subboundaries and are not found in nanograins with high-angle boundaries.

Note that the precipitation of Ti_3Ni_4 particles and the corresponding appearance of the R-phase upon annealing at 400 °C are accompanied by a shift in the characteristic temperatures of martensitic transformation (Table 1). It is consistent with the general regularities of the evolution of the structural-phase state with a change in aging temperature that are obtained for polycrystalline Ni-rich TiNi alloys [2–7,18–20]. At the same time, there are some features of the multistage martensitic transformations in the NC Ti–50.9Ni alloy due to the inhomogeneous Ti_3Ni_4 particles precipitation.

Various hypotheses of the mechanisms of this phenomenon have been proposed [4–7,20]. In polycrystalline TiNi-based alloys, two types of inhomogeneity can change the sequence of martensite transformations: (i) local inhomogeneities of Ni concentrations and internal stresses near coherent Ti_3Ni_4 particles and (ii) microscopic heterogeneity due to the different nature of the decomposition of the B2-solid solution TiNi between the region of grain boundaries and their internal volume [4–7,18,20]. The most probable cause of multistage transformations is the presence of zones differing in size and particle distribution [18]. The inhomogeneity of the distribution of Ti_3Ni_4 particles within the grains provides a difference in the concentration of Ni in the B2-austenite within the boundaries and in the internal volume of the grains. As a result, the B2 \leftrightarrow R transformation first occurs at the

grain boundary with a low Ni content, and then inside the grains with a higher Ni content, which gives rise to the abnormal three-stage martensitic transformation [4–7].

Evidently, the grain size determines the ratio between the volume fractions of grain boundaries and grain volumes and can thus influence the Ti₃Ni₄ distribution and martensite transformations in aged specimens [7,20–22]. Note that according to [23], the size of nickel-depleted zones near the particle-matrix interface varies from 20 to 100 nm, depending on the particle size, which corresponds to the observed range of nanograin sizes and allows considering only local Ni concentration inhomogeneities. Thus, it is unclear what kind of inhomogeneity is responsible for the abnormal three-peak behavior of NC TiNi alloy under intensive aging at 400 °C. At the same time, our analysis identifies inhomogeneities associated with different Ti₃Ni₄ precipitation behavior in substructural regions and groups of nanograins. After aging at 400 °C, the B2 matrix of the Ti-50.9Ni NC alloy exhibits a difference in the Ni concentration in the substructural regions and groups of nanograins, and the scale of this inhomogeneity is much larger than the scale of local stresses and the Ni concentration near Ti₃Ni₄ particles. In this case, an anomalous R-phase transformation effect is possible: higher temperature transformations $B2\leftrightarrow R_1$ in substructural regions with Ti₃Ni₄ particles and lower temperature transformations $B2\leftrightarrow R_2$ in nanograins free of Ti₃Ni₄. This is consistent with the expectation of Ni content depletion in the matrix as Ni-rich precipitation progresses. We believe that the joint occurrence of the two transformation streams is due to the heterogeneity of the grain-subgrain nanostructure of Ti-50.9Ni NC alloy. The study of martensitic transformations by the DSC method made it possible to confirm these assumptions (Figure 5).

5. Conclusions

Electron microscopy analysis of the size and morphology of coherent Ti_3Ni_4 precipitates in grain–subgrain NC Ti-50.9Ni alloy aged at 300 °C and 400 °C is performed.

It was shown that on aging at 300 $^{\circ}$ C, spherical Ti₃Ni₄ particles smaller than 10 nm precipitate at dislocations in the alloy substructure. Such particles are found in dislocation-containing nanograins and are not found in dislocation-free nanograins.

On aging at 400 °C, the Ti₃Ni₄ particles increase in size, changing their shape from spherical to near lenticular and their distribution within the nanostructure from location at dislocations to precipitation at subboundaries. The presence of different types of internal boundaries in Ti-50.9Ni is the main factor that influences the inhomogeneous nucleation of coherent Ti₃Ni₄ particles in the temperature range of their intense precipitation at 400 °C. Such particles nucleate at low-angle sub-boundaries, while decomposition of B2-austenite is not observed in nanograins with high-angle boundaries.

The Ti_3Ni_4 distribution inhomogeneity in NC Ti-50.9Ni provides different structuralphase states in the grain–subgrain nanostructure and accordingly different Ni concentrations in subgrains and nanograins regions. This is one of the driving factors responsible for the occurrence of the anomalous R-phase transformation effect in the sequence of multistage martensitic transformations $B2\leftrightarrow R\leftrightarrow B19'$.

The results reported can help in choosing appropriate thermal and thermomechanical treatment modes for Ni-rich TiNi alloys to improve their performance as cardiovascular implant materials.

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