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EFFECT OF THE COMPOSITION OF A TITANIUM NICKELIDE ALLOY ON ITS STRUCTURE AND ON THE FORMATION OF THE GRAIN BOUNDARY ENSEMBLE

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The structure and features of the grain boundary ensemble in titanium nickelide alloys of different composition have been investigated. Using the methods of scanning electron microscopy, x-ray structure and micro x-ray spectrum analyses, TiNi(B2), TiNi(B19′), Ti_2Ni, Ti_4Ni_2O, *and* $TiNi_3$ *phases have been detected in the alloys and described. The grain structures inherent in alloys of different composition have been systematized and described qualitatively and quantitatively. It has been shown that an increase in* Ni *concentration in the alloys decreases the grain size. The grain size distribution histograms have been constructed, the grain boundary types and morphology have been examined, and the fractions of boundaries of ordinary and special types in the grain boundary ensemble have been estimated for alloys of different composition.*

Keywords: titanium nickelide, martensitic transformation, thermal treatment, grain boundaries, grain boundary ensemble, special grain boundaries.

INTRODUCTION

In polycrystalline materials, where phase transitions are realized, the parameters of martensitic transformations (characteristic temperatures, intervals, transformation hysteresis) depend not only on the external action, temperature, and chemical composition, but (significantly) on the resulting structure and on the grain size of the material parent phase. As the crystallite size and, hence, the intercrystalline boundary volume density are changed, so do both the conditions for the nucleation of martensitic crystals and the pattern of propagation of the martensitic transformation in the polycrystalline ensemble formed. In addition, the martensitic transformation kinetics is affected by the type of the martensite formed and by the structural features of the parent phase [1–11]. As the grain size of a polycrystal is decreased and becomes lower than a certain value, this results in a decrease in the temperature at which a martensitic transformation starts and also in changes in other characteristic temperatures and in the hysteresis of the transformation [12, 13]. A correlation between the grain size, the structural characteristics of the parent phase, and the parameters of the martensitic transformation has been found for various small objects [12–15].

It is also well known that the nucleation of martensitic crystals occurs mostly at the grain boundaries that, by virtue of their atomic structure, possess higher energy compared to the grain bulk [1, 7, 8, 10, 13]. In this case, the grain boundaries not only are the sites of preferential nucleation of martensitic crystals, but they can also impede subsequent crystal growth.

It should be noted that the nucleation and growth of martensitic crystals are significantly affected not only by the grain size, but also by the state of the grain boundaries (grain boundary type), which is characterized by their energy. The proportion between the types of grain boundaries in annealed polycrystalline materials depends on the grain size [16–18].

Review of the results published to date shows a lack of systematic and task-oriented studies of the grain boundary ensemble and of its effect on the martensitic transformations for titanium-nickelide-base alloys. In view of the

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widespread use of titanium nickelide in medicine and engineering, the study of the effect of the composition of a titanium-nickelide-base alloy on the formation of the grain boundary ensemble, on the grain size, and on the type of grain boundaries is of importance.

This work is devoted to the structure of titanium nickelide alloys of different composition, the effect of the alloy composition on the grain size, and the formation of the grain boundary ensemble.

MATERIALS AND INVESTIGATION TECHNIQUES

Investigations were performed for titanium nickelide alloys of different composition: alloys of stochiometric composition, titanium- and nickel-enriched alloys, and technological alloys doped with type TN-10, TN-20, and KhE molybdenum.

$Ti_{48.5}Ni_{51.5-x}$, $Ti_{49}Ni_{51-x}$, $Ti_{49.5}Ni_{50.5-x,}$ and $Ti_{50}Ni_{49-x-1\,\%\ Fe}$ molybdenum-doped alloys were melted with argon blanket in an induction furnace. $Ti_{48.5}Ni_{51.5}$, $Ti_{49}Ni_{51}$, $Ti_{50}Ni_{50,}$ and $Ti_{51}Ni_{49}$ molybdenum-free alloys were obtained by six successive arc meltings in argon blanket. The alloy ingots were rolled into 1 mm thick plates with intermediate annealings in air at a temperature $T = 500$°C.

To produce grain structure, the samples were annealed at 850°C for an hour under 10^{-4} mm Hg vacuum and then slowly cooled in the furnace to room temperature. To perform microstructure analysis, metallographic samples were prepared by a standard method and then the surface was polished. To reveal the grain microstructure, the samples were etched in a solution of $1HNO_3$, 3HF, and $2H_2O$ acids. Macrostructure examination was carried out with an Olympus CX-71 metallographic microscope by the reflection method and differential interference contrast (DIC) analysis.

Examination of the alloy microstructure was carried out in a Philips SEM 513 scanning electron microscope. The phase composition and structural parameters of the alloys were determined by means of x-ray spectrum and structure analyses on an XRD-600 diffractometer.

The grain size was determined by the intercept method. The type of grain boundaries was revealed by optical metallography by their etchability and morphological features. It is well known that ordinary grain boundaries in metals are etched in the majority of electrolytes more severely than special boundaries. By morphological features, all vividly etched curvilinear and rectilinear boundaries were referred to as ordinary boundaries. Weakly etched rectilinear, twin, and faceted boundaries were referred to as special boundaries.

STRUCTURE OF TITANIUM-NICKELIDE-BASE ALLOYS OF DIFFERENT COMPOSITION

Examination of the macro- and microstructure of titanium nickelide samples of different composition after thermal treatment has shown that the main structural feature for all alloys is the presence of phases of different size throughout the sample. The particles are located both along the grain boundaries and in the grain body as separate fine precipitates and as local clusters. However, the particles are mainly localized in the grain body; some boundaries are totally free from precipitates (Fig. 1).

Phase precipitates of different size (0.1–4.2 μm) have been detected. A characteristic feature of the fine precipitates is their regular round shape. Along with individual fine precipitates, larger ones (2.8–4.2 μm) of different geometric shape have been detected. Chain precipitates consisting of individual fine precipitates and local clusters were also observed. It should be noted that on the surface of the samples there were regions with different precipitate distribution densities (from 0.1 to 0.5).

Addition of Mo to titanium-nickelide-base alloys results in a more homogeneous structure. In the alloys with molybdenum additives, mostly fine point precipitates are observed that are uniformly distributed throughout the sample. Only at some places of the matrix, along with fine single precipitates, variously shaped coarser precipitates are observed in small proportion. Like in the undoped alloys, the particles are mainly distributed in the grain body; most of the grain boundaries are free from precipitates (Fig. 2). Local microanalysis has shown that these phases are titanium-enriched particles of the Ti_2Ni type. Based on the phase diagram of TiNi systems, it can be stated that these phases form during

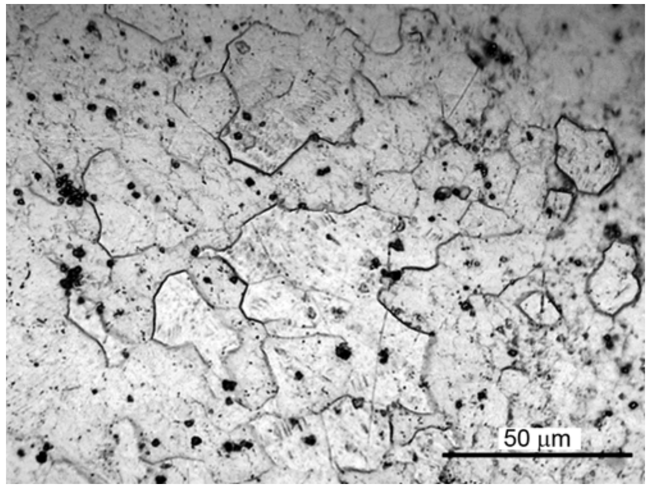

Fig. 1. Macrostructure of $Ti_{49}Ni_{51}$ titanium nickelide alloy after annealing at $T = 850°C$; $t = 1$ h, vacuum.

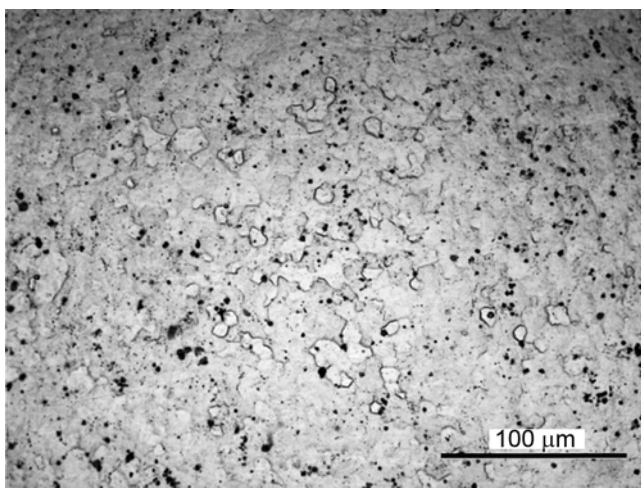

Fig. 2. Macrostructure of titanium nickelide alloys after annealing at $T = 850°C$; $t = 1$ h, vacuum; $Ti_{50.5}Ni_{49.5-x}$ alloy of homogeneous structure.

crystallization, which occurs by the peritectic reaction. Because of the presence of vacancies in the lattice, the TiNi phase has the property of dissolving O, N, and C, which can result in the formation of oxycarbonitrides with composition of the $Ti_4Ni_2(O, N, C)$ type. The Ti_4Ni_2O phase is isomorphic to Ti_2Ni and almost no different from it in lattice parameter ($a = 11.3236$ nm). Rolling of the alloy with intermediate annealings can also give rise to an additional Ti_4Ni_2O phase precipitate due to active penetration of oxygen and its interaction with titanium.

The data of x-ray diffraction analysis for all alloys confirmed the presence of the Ti_2Ni, Ti_4Ni_2O, and $TiNi_3$ phases in addition to the TiNi phase in the B2 and B19′ states in all samples irrespective of the composition.

Particles of Ti_4Ni_2O titanium oxides have a lamellar, round or regular rhombic shape (Fig. 3). It must be emphasized that the titanium-enriched particles of the Ti_2Ni type observed in the titanium-enriched alloys were coarser and the density of precipitates was greater compared to this type of particles in nickel-enriched alloys. Besides, in addition to Ti_2Ni precipitates, fine phases were detected in the form of light precipitates mainly of round and lamellar shape. X-ray spectrum analysis has shown that these were nickel-enriched $TiNi_3$-type phases. The particles of this phase are fine-dispersed (0.1 μm or smaller in size) and have a coherent match with the matrix. They can be located both at

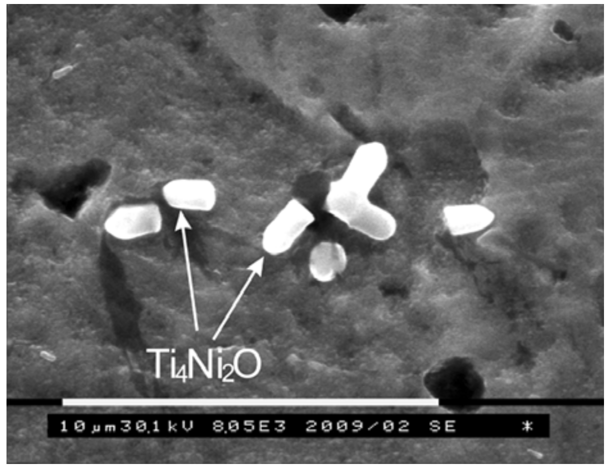

Fig. 3. Microstructure of $Ti_{49.5}Ni_{50.5}$ titanium nickelide alloys after annealing at $T = 850°C$; $t = 1$ h, vacuum; titanium-enriched phases.

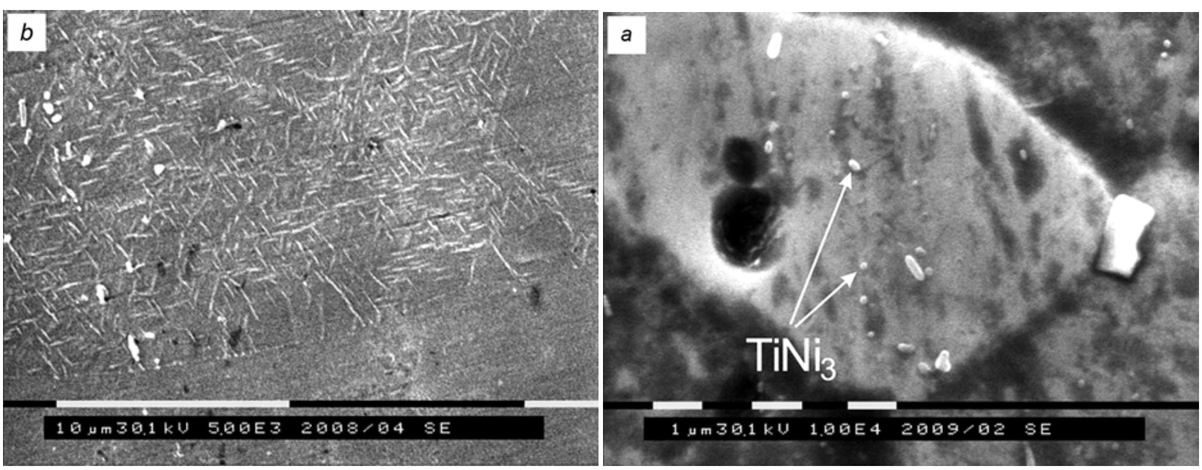

Fig. 4. Microstructure of titanium nickelide alloys after annealing at $T = 850°C$; $t = 1$ h, vacuum; nickel-enriched phases: round and lamellar (*a*) and network type (*b*).

grain boundaries and in the grain body (Fig. 4*a*). The data of x-ray diffraction analysis also confirmed the presence of $TiNi_3$ phases and showed that the volume fraction of the nickel-enriched phases in the alloys was much smaller than that of the titanium-enriched phases.

Coarser lamellar precipitates (0.4–0.5 µm in length and about 0.1 µm in width) were observed at many places of the highly nickel-enriched alloy matrix. By analogy with the data available in the literature, one may suppose that these can be type Ti_2Ni_3 particles, as it is well known that intermediate metastable nickel-enriched phases, coarser lamellar Ti_2Ni_3 precipitates, and lenticular Ti_3Ni_4 and $Ti_{11}Ni_{14}$ particles can form in the matrix during annealing in addition to the $TiNi_3$ phases [24].

In the alloys enriched in nickel, high density of $TiNi_3$ precipitates arranged as a network has been detected at some places of the matrix (Fig. 4*b*). These precipitates could form both during deformation and heat treatment and during annealing.

Thus, it has been shown that identical structures with some features in the density distribution and in the size of the precipitated phases and their clusters are formed in titanium-nickelide-base alloys of different composition. In the alloys doped with molybdenum, a more homogeneous structure with a preferential distribution of particles in the grain

TABLE 1. The Average Grain Size of Titanium Nickelide Alloys

Alloy	$Ti_{50.5}Ni_{49.5}$	$Ti_{50}Ni_{50}$	$Ti_{49}Ni_{51}$	$Ti_{48.5}Ni_{51.5}$
d, μm	35	30	23	9

TABLE 2. The Average Grain Size of Mo-Doped Titanium Nickelide Alloys

Alloy	$Ti_{50}Ni_{49-x}$	$Ti_{49.5}Ni_{50.5-x}$	$Ti_{49}Ni_{51-x}$	$Ti_{48.5}Ni_{51.5-x}$
d, μm	12	17	23	23

body is observed. The data of x-ray diffraction and micro x-ray spectrum analyses have shown that intermetallic compounds, such as TiNi, Ti_2Ni, Ti_4Ni_2O, and $TiNi_3$ form mainly in alloys of this type.

SPECIFIC FEATURES OF THE GRAIN BOUNDARY ENSEMBLE IN TITANIUM-NICKELIDE-BASE ALLOYS OF DIFFERENT COMPOSITION

The formation of the grain boundary ensemble in metals and alloys depends on many factors, such as the temperature and strain before thermal treatment, the thermal treatment mode, the stacking fault energy, and the presence of doping and impurity elements [18–22].

The grain boundary ensemble in titanium-nickelide-base alloys of different composition was examined using optical metallography and scanning electron microscopy. A qualitative and quantitative description of the grain structure was performed.

The type of grain boundaries was determined by the method of differential grain boundary etching. The degree of etching is determined by the grain boundary energy. As ordinary grain boundaries have a greater energy than special type boundaries, they are etched more severely in the majority of electrolytes [17, 18, 20].

In titanium nickelide alloys of different composition, after annealing at $T = 850°C$ for an hour, a grain boundary structure forms whose grain size is presented in Tables 1 and 2.

It has been found that the average grain size in the alloys decreased from 35 to 9 mm with increasing nickel concentration (Table 1). This can be explained by the fact that in these alloys, as shown above, coherent $TiNi_3$-type nickel-enriched phases precipitate. These phases, owing to their fineness and coherent match with the matrix, initiate internal stresses in the material and inhibit grain growth. The effect of the Mo doping element levels off the material microstructure and, hence, promotes uniform grain growth (Table 2).

Figure 5 presents histograms of the grain size distribution for different alloys. Examination of the histograms shows that a normal grain size distribution is typical of all alloys. The grain size distribution is highly nonuniform. This is related to the internal state of the material during crystallization and to the influence of the developing structure on grain growth.

The grain boundaries were categorized according to morphological characteristics by selecting ordinary-type and special-type boundaries. In the course of examination, straight, curved, twin, and faceted boundaries have been detected. Facets are flat sections forming sharp bends in the boundary track on a metallographic section, and they are arranged in specific crystallographic planes, providing the best match between the lattices for a given misorientation [9, 17, 21, 22].

The grain-boundary ensembles formed in alloys of different composition under the same heat treatment are dissimilar; the ordinary grain boundaries can be both curved and straight and the special grain boundaries can be straight, faceted, and twin (Fig. 6).

It is well known that the formation of special grain boundaries is determined by the migration ability of the ordinary grain boundaries and by the intensity of recrystallization processes because of the splitting of the ordinary grain boundaries as a way to reduce the grain boundary energy of the polycrystal [18]. The migration ability of ordinary grain boundaries in single phase solid solutions depends on the stacking fault energy and on the concentration of alloying elements in the solid solution, whereas that in multiphase alloys is governed by the presence of the second

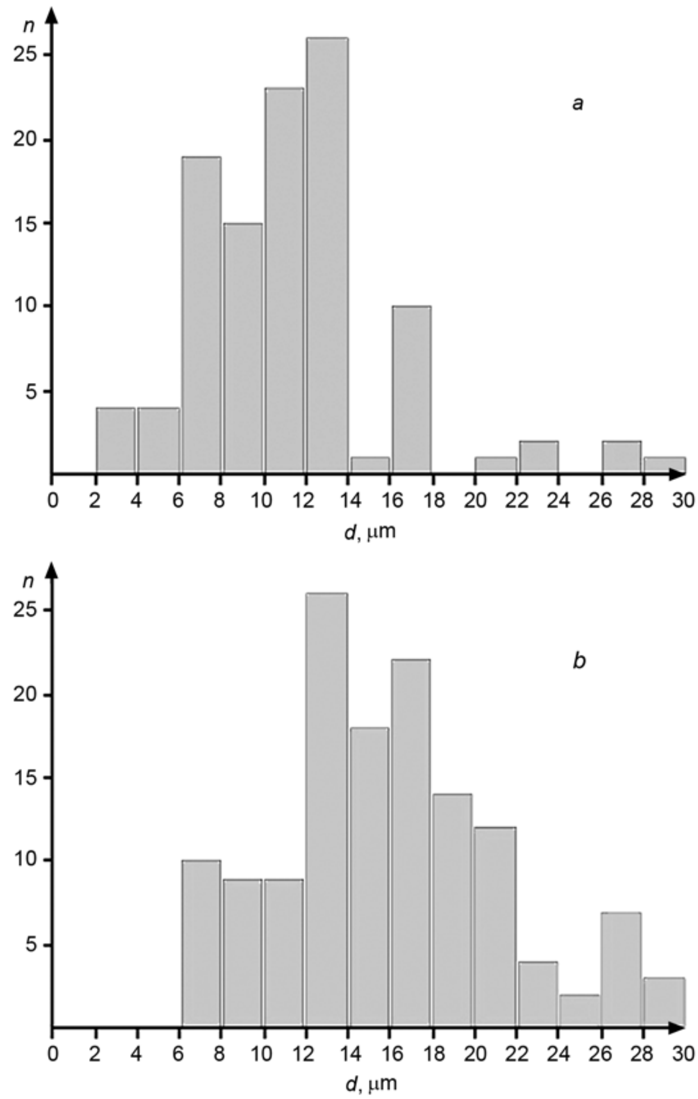

Fig. 5. Grain size distribution histograms for $Ti_{49.5}Ni_{50.5-x}$ (*a*) and $Ti_{49}Ni_{51}$ titanium nickelide alloys (*b*).

phases at grain boundaries. The intensity of the recrystallization processes is determined by the annealing mode and temperature and by the kinetics of structure formation.

Special-type boundaries are almost always free of precipitates. This is due to their low energy. It is well known from the literature that the energy of grain boundaries of the Σ 8, 38, 94 special type is 0.3 of the energy of ordinary grain boundaries [13, 17, 18, 22]. Quantitative analysis of the proportions between grain boundaries of different types in the alloys investigated has shown that the fraction of special boundaries in the grain-boundary ensemble is 0.3–0.5 of the total number of boundaries (Tables 3 and 4).

It is well known that the number of special grain boundaries in annealed polycrystalline metals and alloys depends on the grain size. However, this dependence is ambiguous for different materials. Thus, it has been shown that the percentage of special grain boundaries in silicon polycrystals is 50% for a grain size up to 20 μm and 100% for a grain size of 2 μm [15].

Analysis of the results obtained has shown that the percentage of special-type boundaries in the nickel-enriched titanium nickelide alloys with the smallest grain size, d = 9 μm was 51.4%. As the grain size was increased to 35 μm,

TABLE 3. Percentage of Boundaries of Different Types in Titanium Nickelide Alloys

Alloy	$Ti_{50.5}Ni_{49.5}$	$Ti_{50}Ni_{50}$	$Ti_{49}Ni_{51}$	$Ti_{48.5}Ni_{51.5}$
Ordinary boundaries, %	59.1	51.3	62.6	48.6
Special boundaries, %	40.9	48.7	37.3	51.4

TABLE 4. Percentage of Boundaries of Different Types in Mo-Doped Titanium Nickelide Alloys

Alloy	$Ti_{50}Ni_{49-x}$	$Ti_{49.5}Ni_{50.5-x}$	$Ti_{49}Ni_{51-x}$	$Ti_{48.5}Ni_{51.5-x}$
Ordinary boundaries, %	66.7	47.4	62.9	54.1
Special boundaries, %	33.2	52.6	37.1	45.9

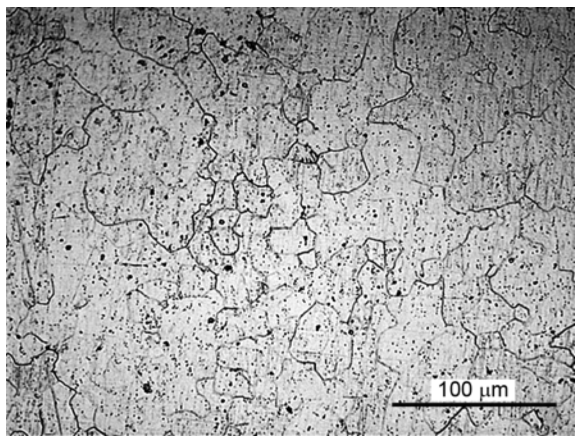

Fig. 6. Macrostructure of $Ti_{48.5}Ni_{51.5}$ titanium nickelide alloy after annealing at $T = 850^{o}C$; $t = 1$ h, vacuum; boundaries of the ordinary and special types.

the percentage of special-type boundaries decreased to 40.9% (Table 3). Doping titanium nickelide alloys of different composition with Mo reduced the grain size and stabilized the alloy structure. The proportion between the special and the ordinary boundaries both in the doped and in the undoped alloys slightly varied (Table 3 and 4).

It has been shown that the fraction of special grain boundaries in alloys with molybdenum additives increased from 0.3 to 0.5 with increasing Ni concentration.

CONCLUSION

Analysis of the structural features of titanium nickelide alloys of different composition has revealed that the alloys contain TiNi(B2), TiNi(B19′), Ti_2Ni, Ti_4Ni_2O, and $TiNi_3$ phases. The titanium-enriched phases are incoherent and vary in shape from round to rhombohedral, their size varying from 0.1 to 4 μm. The $TiNi_3$ phases, 0.1–0.2 μm in size, are fine-dispersed, coherently matched with the matrix, and mainly localized in the grain body. Adding Mo to the titanium-nickelide-base alloys gave rise to a more homogeneous structure. As the Ni concentration in the alloys was increased from 49.5 to 51.5 at. %, the grain size decreased from 35 to 9 μm. Decreasing grain size in undoped alloys increased the percentage of special-type grain boundaries. The grain size in alloys with different additives of Mo and Fe varied insignificantly. It has been found that the grain boundary ensemble formed in alloys of different composition after thermal treatment at $T = 850°C$ for $t = 1$ h varied from alloy to alloy. The fraction of special-type boundaries in the grain boundary ensemble of the alloys was 0.3–0.5 of the total number of boundaries. The doping elements changed the proportion between ordinary and special grain boundaries in the structure of the alloys insignificantly.

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