SECTION 3. Nanotechnology. Physics.

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INFLUENCE OF THERMAL TREATMENT ON STRUCTURAL TRANSFORMATIONS IN Ti-Ni ALLOYS

Abstract: *The work includes the experimental results of the study of two groups of alloys of Ti-Ni system with a shape memory effect by electron microscopy and resistometric measurement. A high dislocation density was found after high-temperature treatment. It is established that new precipitations exist only in a certain temperature range.*
Key words: *transition metals, titanium, nickel, alloy, structure, phases, martensitic transformations, shape memory effect.*
Language: *English*

Introduction

Since olden times the researchers have been very interested in two- and three-component alloys of transition metals that have the ability to restore their shape when heated, as a result of prior deformation. This phenomenon, called the *shape memory effect*, is associated with the martensitic transformation process, occurring in the alloy as a result of heating within a certain temperature range.

Among variety of similar materials Ti-Ni alloys have a number of advantages in comparison with others, where the shape memory effect is determined. These materials have the ability to completely restore the given shape when heated, and also have good plasticity, sufficient heat resistance and improved corrosion resistance. Despite a significant number of studies devoted to these alloys, where the changes in mechanical and physical properties, the influence of thermomechanical treatment on transformation processes, the structural changes in initial and martensitic phases were studied, a clear picture of phase transformations occurring there, and the reasons of changes in various properties were not obtained, and, most importantly, the results reached by different authors were often difficult to compare. The main reason for these failures was the impossibility of alloying under strictly identical conditions. It is known that it is extremely difficult to obtain two fusions of TiNi alloys of the same composition with the same properties. Therefore, it seems appropriate to carry out researches to obtain data on structural and phase transformations in alloys under various external influences and influence of thermal treatment on subsequent martensitic transformation.

Phase transformations in Ti-Ni allows. A general chart of Ti-Ni system state is shown on the figure 1. Three types of compounds are possible in the system: Ti_2Ni, $TiNi$, $TiNi_3$. The first Ti_2Ni compound is formed in peritectic reaction and has a homogeneity range. At a temperature of 7000°C the homogeneity range is ~ 2 at.% and it slightly narrows under temperature decrease. The TiNi compound crystallizes from the fusion at 1310°C. Under temperature decrease it dissolves a certain amount of Ni in Ti, which leads to the formation of homogeneity range. The maximum homogeneity range of this alloy extends within the range of 49.5 ÷ 57 at.% Ni at a temperature $T = 1118^0 C$. It is assumed that at a temperature $T \prec 630^0 C$ this alloy eutectoidly dissolved into a compound of two phases, consisting of Ti_2Ni and $TiNi_3$. The $TiNi_3$ compound melts congruently at

13800°C. In Ti-Ni system there are three eutectic, one peritectic and one eutectoid transformations.
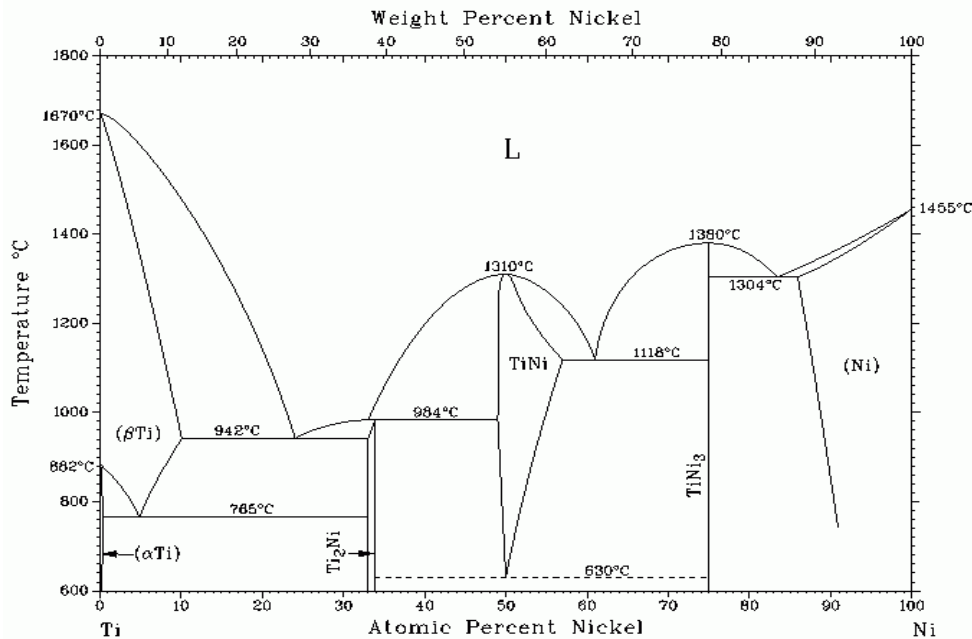

Figure 1 - Chart of Ti-Ni alloys system state.

In Ti-Ni alloys the martensitic transformation occurs in a narrow concentration range near the equiatomic composition of Ti-50 at.% Ni. The high-temperature phase of TiNi (β, BCC, $a = 0.302$ nm) at a room temperature exists in a narrow concentration range (~ 0.5 at.%) [1]. A compound of two phases Ti_2 $Ni + TiNi$ is formed at lower Ni content (≤ 50 at.%) and at a temperature of 1015°C. A compound of $TiNi + TiNi_3$ is formed under high Ni concentrations (> 50 at.%) at a temperature below 1100°C. Ti_2Ni compound has a complicated face-centered cubic lattice - lattice with the parameter $a = 1.131$ nm. It contains 96 atoms, whereas $TiNi_3$ has a hexagonal lattice with the parameters $a = 0.509$ nm and $c = 0.831$ nm, containing 12 atoms [2].

A large number of works are devoted to the study of the crystal structure of phases arising in TiNi alloys near equiatomic composition at a temperature range of 800°C. And, interestingly, that the results of these studies are interpreted in different ways. For example, the work [2] reports about three phase states in alloys Ti-51 at.% Ni. It is believed that in the temperature range above 700°C there is TiNi phase (I) with BCC structure and the parameter $a = 0.3$ nm. Within the interval (600 ± 40°C) an ordered phase TiNi (II) appears with the BBC lattice parameter $a = 0.9$ nm and 54 atoms per cell. This cell is represented as the set of two simple cubic lattices with coordinates of atoms (000) and (½, ½, ½) and the sequence of arrangement of Ti-Ti-Ni-Ti-Ti and Ni-Ni-Ti-Ni-Ni atoms, respectively. The TiNi (II) alloy undergoes a diffusionless pseudomartensitic transition at a

temperature of 166°C. At that the work denies possibility of TiNi and $TiNi_3$ phase breaking. The martensitic phase of TiNi (III) is formed at a temperature below 400°C. Another model of the BCC lattice with the parameter $a = 0.903$ nm was presented in the work [3]. In essence it differs from the previous one only by a different alternation of Ni and Ti atoms. On the basis of electronic and diffraction studies the work [4] proposes to describe this phase by a rhombohedral structure with a parameter $a = 0.903$ nm at an angle $\alpha_{min} = 89.3^0$. On electron microscopic images, obtained in reflexes [5], located at distances of 1/3 between the main ones, thin domains - *precipitations* are visible. These precipitations are found in samples in annealed and slowly cooled conditions.

The work [6] assumes that the high-temperature TiNi phase decay into Ti_2Ni and $TiNi_3$ occurs in equiatomic alloys under $T = 650^0 C$. According to the authors of the work [6] a plastic-like Ni_3Ti_2 phase with a hexagonal lattice with the parameter $a = 0.27$ nm, $c = 0.44$ nm and $c/a = 1.63$ nm is formed in the hypereutectoid alloy (52 at.% Ni) upon annealing during 1 month at $T = 660^0 C$. This structure is an intermediate one between two types of Ti_3Ni phases: *widmanstatten and equiaxial.*

The crystalline structure of martensite was determined in many works, including [7]. It was found that martensite has a close-packed structure, but the alternation and number of close-packed layers in one period, determined by different authors, is different.

The formation of martensite with a triclinic lattice was reported in the works [8]. Moreover, these works show various values of the lattice parameters. It is most often assumed that martensite in TiNi alloys has a monoclinic structure of β' type. It is also known that martensitic transformation in Ti-Ni alloys is a first-kind transformation and it occurs thermoelastically [9]. In martensitic transformation in TiNi alloys, a relief appears on the polished surface. The martensite crystals grow with lowering of temperature and decrease its size with rising temperature. The thermal hysteresis does not exceed 25-30° C. Such a hysteresis value apparently depends on small volume changes under transformation (0.16%). The dislocation density increases when the reverse transformation occurs in the initial phase.

Martensite is formed in the shape of alternating plates with two orientations with a common boundary along ($\bar{1}1\bar{1}$)$_m$ [10]. The adjacent plates have a width of 100 and 200 nm and differ in the direction of $^{//}c^{//}$ and $^{//}a^{//}$ axes. Three morphological types of martensite were observed in the alloy Ti-50.1 at.% Ni: lamellar, massive and tortuous [11]. A lamellar martensite contains stacking defects located at a distance of 3-6 nm from each other. In addition to stacking defects in martensite there were also found twins of ($\bar{1}1\bar{1}$)$_m$. type.

Methods of research. Hot soaking often leads to a change in the structural state of both the initial martensite phase and the subsequent martensite phase that is formed after cooling. After such treatment the appearance and distribution of dislocation and vacancy defects can be different. At the same time the degree of order and the degree of decomposition of the initial solid solution, as well as the phase composition of the material, can differ. In addition, various physical and mechanical properties can change. In view of this, it follows that it is extremely important to conduct studies on the influence of various thermal and thermomechanical treatments on structural and phase changes in Ti-Ni alloys, obtained under identical conditions.

The studies were carried out on alloys of Ti - (50-60) wt.% Ni. The alloys were melted in vacuum by the arc melting method with a threefold Ti and Ni remelting of 99.99% purity. The obtained ingots were rolled in air at $T \succ 600^0 C$ to the thickness of 0.6÷1.0 mm. The rolled plates were kept at $T = 1000^0 C$ for 15-30 minutes, followed by quenching in NaOH alkali water. Thermal treatment was carried out in argon medium according to the scheme:

а) Quenching at 1000°C, heating and holding in a given temperature range (200-800) 0C for a certain time.

б) Rapid cooling at 1000°C to the given temperature (200-800) 0C and holding for a certain time.

Investigation of structural and phase changes, occurring in the material after various treatments, was carried out by electron microscopy and resistometric measurements.

Discussion of the results. The high dislocation density and elongated subgrains with the dimensions (0.3-0.5) x (3÷5) µm were found in the samples after high-temperature rolling, providing blurring of reflexes on micro-diffraction patterns into rings and arcs. Holding and quenching at 1000°C lead to the removal of defects (dislocations), recrystallization process and growth of new grains. After such treatment large grains of high-temperature β - phase are visible on microstructural images. Inside these grains a «*mottling*» is detected, which is apparently specified by dispersed precipitations of another phase and particles of Ti$_2$Ni phase, which are located both inside the grains and along the boundaries. The «*mottling*» in β - phase, observed after quenching at 1000°C, becomes much clearer after holding at 200-500°C and cooling to the room temperature. There were no other changes in the microstructure. Probably, such structure is specified by small particles (~ 3-10) nm of the new phase formed during aging.

Certain microstructural changes of the following character become viseable after holding at 300 ÷ 4000 °C: dislocation loops and individual deformation contrast around discrete precipitations are detected. Fine (up to 0.2 µm) particles of the x − phase of $\prec 110 \succ_\beta$ type are clearly visible on dark-field images. Prolonged holding (up to 300 min) leads to an increase of these particles to ~ 0.5 µm in the longitudinal direction. The particles take the form of elongated lenticular (pointed at both ends) plates, coherent with the surrounding matrix. In later stages of growth (~ 5000 ° C), when the particles reach considerable dimensions, they consist of several parts with different orientation, which is detected by alternation of light and dark areas. These areas are often separated by a clear boundary. When they are small (up to 0.5 µm) the particles have a light thickness. This is shown by streaky contrast at the boundaries of x − particle and β - phase.

The particles interact in the process of growth. If one of them strikes upon the other, its growth stops in this direction, but it grows in thickness. At the same time a large particle absorbs small ones without forming new boundaries inside a large particle, whereas old boundaries disappear. Often it is possible to detect 2-3 orientations of x − particles in the neighborhood.

With increase of holding time and temperature (up to 550-650°C) the plates of x − phase grow in length and in thickness (Fig. 2). As a result, a coherence violation occurs, which leads to imperfect dislocations on interphase boundaries (between β - and x − particles), located at a distance of 75-80 nm from each other. Similar structural changes are observed after

treatment according to the second scheme, i.e. after heating and holding for quenching and subsequent cooling to a given temperature within the range of 800 ÷ 500°C. It should be noted that x – phase exists up to the temperature of 650-700°C. Above this temperature the particles and the reflections of x – phase disappear. On micro diffraction patterns there are diffuse reflexes

of β –phase. The intensity of these phases declines as the temperature rises. Thus, the x – phase exists in a certain temperature range, above and below which it cannot exist. The amount of this phase does not exceed 10-15%.
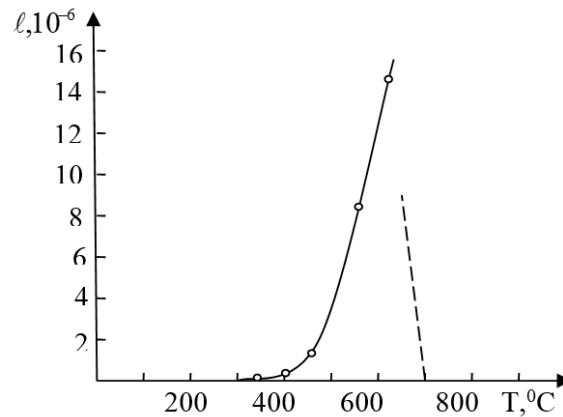

Figure 2 - Dependence of particle size of x -phase in TiNi alloy on the holding temperature
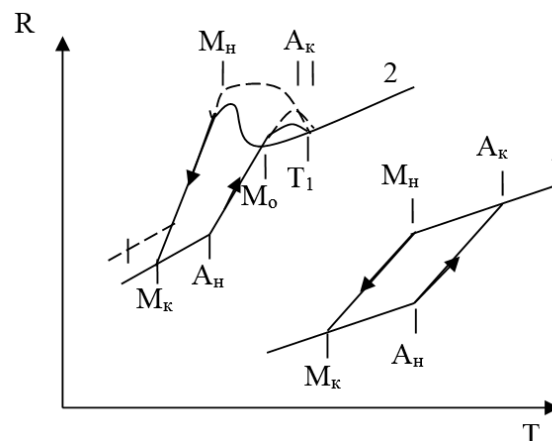

Figure 3 - Temperature dependence on electrical resistivity (ΔR) in TiNi alloy

The electrical resistivity method is often used to record the flow of the martensitic transformation process in the material. This method allows to determine the martensitic points ($M_н$, $M_к$, $A_н$, $A_к$) and thermal hysteresis with high accuracy, and also to monitor the intermediate stages and transformation kinetics. In alloys TiNi, as in the case of martensitic transformation, there is the decrease of electrical resistivity (Fig. 3). However, in the works [9] prior to decrease in electrical resistivity under temperature lowering, a rise was observed, which corresponds to a negative coefficient of electrical resistance. With a temperature cycling in a certain interval, where a partial reverse transformation occurs, the height of the peak increases, and the temperature interval of its

appearance shifts to the lower temperature range. Therefore, it is attractive for study of the influence of thermal treatment at elevated temperatures on the magnitude and position of the peak (if it exists), the dependence of its occurrence on concentration of elements in the alloy, and the development of structural changes that cause its occurrence.

It was found that the electrical resistivity dependence on temperature for TiNi alloys is determined by the composition [12]. This dependence is usual in the alloys of A1 group (containing 53.7 ÷ 55.0 wt.% Ni) (Fig. 3 curve 1). Upon cooling and heating the hysteresis loop, specified by martensitic transformation, is observed in the change in electrical resistivity. The value of the electrical resistivity does

not practically change after holding for 300 min. in the interval 200-800°C (Fig. 4, curve A).

Under temperature cycling through the martensitic transformation area the shape of curves does not change, but this leads to a slight decrease in the value of M_n point (after 10 cycles).

A different dependence of the electrical resistivity on temperature is observed in the alloys of B1 group (containing 56.4 wt.% Ni) (Fig. 3, curve 2). Prior to the drop in electrical resistivity due to martensitic transformation, there is a rise beginning at a temperature M_0 and ending at a temperature corresponding to M_n point. An ordinary drop in electrical resistivity is observed below this temperature. The ratio of the magnitude of the peak to the change in the electrical resistivity due to martensitic transformation of quenched samples is 5÷10% and depends on the composition of the alloy.

A peak is also observed on $R(T)$ curve when heated, but its value is much smaller and it is shifted to higher temperatures by $0 \div 20$°C. Temperature cycling leads to decrease in the value of M_n point in samples, held at elevated temperatures, and to increase in the peak by a factor of 2÷3. The peak value is strongly influenced by the holding temperature at a fixed time. As the temperature rises the peak value increases and at 450-500°C it reaches its highest value, and then sharply decreases (Fig. 3c). After holding at 550°C and more the electrical resistivity is the same as in the quenched samples.
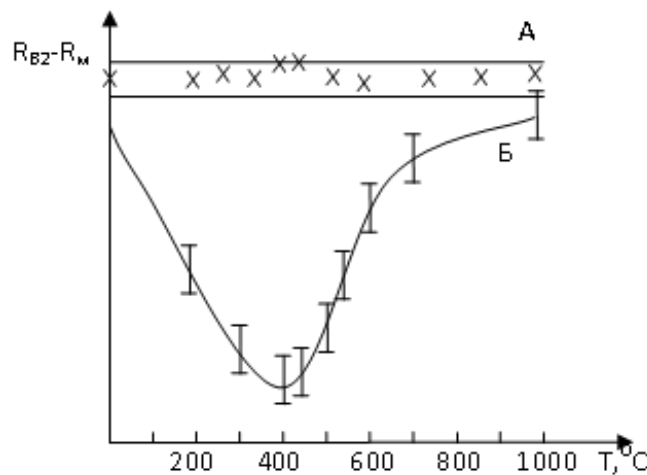

Figure 4 - Influence of holding temperature on the break jump of electrical resistivity in martensitic transformation (RB2-Rm) in TiNi alloys of A and B groups
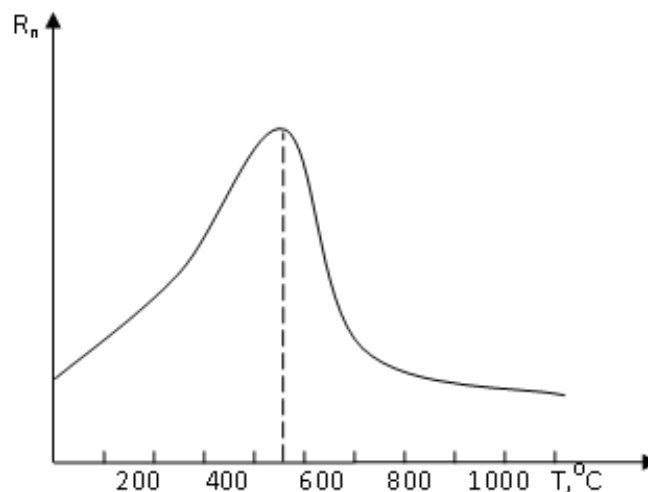

Figure 5 - Temperature dependence of additional peak value of electrical resistivity in TiNi alloy

Conclusions.

The effects found in Ti-Ni alloys are substantiated by premartensitic instability, which

causes vibrations of atoms along certain crystal directions, which near the temperature point of martensitic transformation of M_n leads to the appearance of plane waves. The martensite crystals grow with lowering temperature and decrease with rising temperature. Thermal hysteresis does not exceed 25-30°C. Such hysteresis is probably specified by small volume changes ($\sim 0.16\%$).

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References:

1. Kornilov II, Belousov OK, Kachur YV (1977) Titanium nickelide and other alloys with memory effect. –M.. p. 179.
2. Wang FE, Buchler WJ, Pickart SJ (1965) Crystal structure and unique «martensitic» transformation of TiNi // J.Appl. Phys. 36. p. 3232-3239.
3. Nagasawa A (1970) A new phase transformation in NiTi alloy. // J.Phys. Soc. Jap. 29. p. 1386.
4. Nagasawa A (1970) A new phase transformation in NiTi alloy. // J.Phys. Soc. Jap. 1970. 29. p. 1386.
5. Gupta SP (1974) The transition phase in near-equiatomic Ti- Ni alloy // Mater. Sci. and Eng.. 14. p.157-168
6. Gupta SP, Mukherjee K, Johnson AA (1973) Diffusion Controlled Solid state transformation in the near-equiatomic Ti-Ni alloys. // Mater. Sci. and Eng. 1973. 11. p. 283-297.
7. Nagasawa A, Maki T, Kakinoki J (1969) Close packed layer structures of NiTi martensite // J. Phys. Soc. Jap.. 26. p. 1560.
8. Dautovich DP, Purdy GR (1965) Phase transformation in TiNi. // Can. Met. Quart.. V. 4. p. 129-148.
9. Otsuka K, Sawamura T, Shimizu K, Wayman CM (1971) Characteristics of the martensitic transformation in TiNi and memory effect // Met. Trans. V. 2. p. 2583-2588.
10. Gupta SP, Johnson AA (1973) Morfology and crystallography of β' – martensite in TiNi alloys // Trans. Jap. Inst. Metals. V.14. p. 292-302.
11. Lobodyuk VA (1980) Shape memory effect and fine structure of martensite – Kiev: RDENTP. p. 26.
12. Koval YN, Kolomytsev VI, Lobodyuk VA, Martynov VV, Khandros LG (1979) Influence of thermal treatment on the shape memory effect in Ti-Ni alloys // In the book. Martensitic transformations in metals and alloys. - Kiev: Naukova - Dumka. p. 145-150.