Metallophysics and Advanced Technologies
Металофіз. новітні технол.
Metallofiz. Noveishie Tekhnol.
2023, vol. 45, No. 11, pp. 1293–1309
https://doi.org/10.15407/mfint.45.11.1293
Reprints available directly from the publisher

PACS numbers: 07.05.Kf, 61.50.Ks, 61.72.Ff, 62.20.fg, 64.70.kd, 64.75.-g, 81.30.Kf

The Relationship between Chemical Composition of the Alloy and the Parameters of the Martensitic Transformation in NiTi Alloys

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Today, shape-memory alloys have already taken their place in various fields of science and technology. The most used alloy is titanium nickel or nitinol. When manufacturing alloys based on NiTi in order to use them for various products, it is necessary to know the conditions, under which it is possible to obtain alloys with previously known parameters of the phase transformation. In the work, the dependence between the Ni/Ti ratio, preliminary thermomechanical treatment (TMT) and the temperature of the beginning of the martensitic transformation (M_s) is obtained.

Key words: direct and reverse transformations, shape-memory effect, vacuum induction melting, vacuum arc melting, additive methods.

Нині стопи з пам'яттю форми вже зайняли своє місце в різних галузях науки та техніки. Найбільш використовуваним є нікелід титану або нітинол (NiTi). Для виготовлення стопів на основі NiTi потрібно знати умови, за яких можна одержати стопи із заздалегідь відомими параметрами фазового перетворення, чому і присвячено дану статтю. В роботі одержано залежність між співвідношенням Ni/Ti, попереднім термомеханічним обробленням (ТМО) та температурою початку мартенситного перетворення (M_s).

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Citation: Yu. M. Koval, V. V. Odnosum, T. G. Sych, G. S. Mogylnyy, V. V. Burtsev, and A. Yu. Sezonenko, The Relationship between Chemical Composition of the Alloy and the Parameters of the Martensitic Transformation in NiTi Alloys, *Metallofiz. Noveishie Tekhnol.*, **45**, No. 11: 1293–1309 (2023). DOI: 10.15407/mfint.45.11.1293

Ключові слова: пряме й обернене перетворення, ефект пам'яті форми, вакуумна індукційна плавка, вакуумна дугова плавка, адитивні методи.

(Received 13 October, 2023; in final version, 14 November, 2023)

1. INTRODUCTION

Today, the industrial production of nitinol is carried out using two traditional methods of melting, namely vacuum induction melting (VIP) and vacuum arc melting (VAM). The best generalization of the traditional production process is given in [1]. The most modern methods, namely, selective laser melting and production of nitinol using additive manufacturing are described in [2] and [3], respectively. Induction melting allows obtaining homogeneous samples. However, it is necessary to conduct an analysis of both pure components and final castings for oxygen and carbon content [1], since melting is performed in copper water-cooled or graphite crucibles. For example, NiTiMet Company Group [4] in the material posted on the website claims that the optimal conditions for obtaining TH1 and TH1-НК nitinol (which is used in medicine) are the presence of a vacuum with a residual gas pressure of 0.0001 mm Hg, the melting itself should be carried out in vacuum-arc furnaces with a consumable electrode, vacuum-arc crucible furnaces with a non-consumable electrode, vacuum furnaces with induction heating (which provide garnish melting), electron beam furnaces, plasma arc furnaces. According to [1], the most harmful impurities in nitinol castings are carbides and oxides. Samples after VAM are considered cleaner. After smelting, the next step in casting processing is the destruction of the cast structure. Such destruction occurs due to heat treatment using hot deformation at temperatures of 850–950°C, and then, cold deformation is carried out with the aim of obtaining a product or semi-finished product (rolled sheets or wire).

According to [1], the process of processing a cast nitinol sample is as follows: 1) hot deformation process (rolling, extrusion) at a temperature of 850–950°C. After it, the sample is cooled in air; 2) the cold deformation process, which consists of two parts: the first is the cold deformation itself (cold rolling or obtaining the wire by drawing through the dies, and the degree of deformation can reach 45%), and the second is a specific heat treatment after the cold deformation process.

Thus, the first stage is the production of the casting; the next step is the thermomechanical processing of the casting in order to obtain rolled steel, wire, and tubes. In addition, powders for the production of various products can be produced from castings in various ways using powder metallurgy methods. It should also be noted that nitinol powder is used for 3*D* printing [5].

Schematically, the technology for the production of nitinol semi-finished products can be represented according to the scheme: melting + thermomechanical treatment (rolling + heat treatment).

An important position for controlling the acquisition of the required properties is the maintenance of the given ratio between nickel and titanium (Ni/Ti). According to the considerations presented by the authors [1], a deviation of 0.1 at.% in the Ni/Ti ratio causes a deviation in the transformation temperatures by 5–10°C. In order to use a nitinol product for the needs of the human body, it is sometimes necessary to ensure the accuracy of the transformation temperatures up to 2°C.

In electrical engineering and cybernetics, the 'black box' method is used [6]. The production of nitinol, or another alloy with shape memory, can be imagined as a black 'box system'. Such systems have an 'input' for inputting information and an 'output' for displaying work results. The state of the outputs usually functionally depends on the state of the inputs. If the working mechanism is not important, then, the dependence of the results on the input data is usually known; the concept of a 'black box' is used in order not to be distracted by the internal structure. We are going to assume that the ratio between the components is an input parameter, and the characteristic temperature of the beginning of the direct transformation, respectively, is the output. Thus, the task of obtaining a semi-finished product with predetermined values of functional properties is reduced to establishing a relationship between input and output parameters. The semi-finished product production scheme, based on the 'black box', will look like in Fig. 1. Analysis of the behaviour of the connection between the input of the 'black box' and the output is the 'model of nitinol production'. Moreover, a mathematical model are described such a relationship between input and output parameters. This model reflects the production process. According to [6], the equation can be considered as such a model:

$$y = \varphi(x), \tag{1}$$

where y is the output parameter: the temperature of the beginning of the martensitic transformation of M_s [°C], and x is the input parameter: the ratio between Ni/Ti.

Fig. 1. Scheme of the 'black box' for the production of nitinol.

The main goal of this work is to establish the appearance of a mathematical model of the connection between input and output, or a model that describes the influence of the ratio between alloy elements and the temperature parameter of the martensitic transformation.

The issue of predicting phase transformation parameters taking into account changes in chemical composition and various thermomechanical developments is described in [7].

In [7], the authors used an interpreted boosting surrogate model of machine learning (ML) to predict the characteristic transformation temperatures in alloys that exhibit the shape-memory effect, and the prediction accuracy is 95%. The authors of this work also take into account the influence of heat treatment of the rolled samples of alloys, extrusion parameters on the transformation parameters in the alloy. With the help of Shapley values, the influence of the importance of these parameters on the transformation temperature has a certain quantitative assessment. The value of the article [7] is that the authors carried out a quantitative assessment of the influence of various parameters on the transformation temperature, and determined the 'weighted importance' of each factor in relation to the transformation temperature. In this way, the authors predict alloys that demonstrate the ability to restore shape. It should also be noted the analysis of the problem of 'discovery of new alloys that are able to restore shape', conducted by the authors of this work. They argue that when studying alloys, the 'traditional discovery' consists in working within a system of compromises, namely, to obtain some characteristics, we degrade others. When creating an alloy, the optimal composition is soughed according to the principle: we select the elements to provide the property that we consider the main one, but greatly suppress others. A brief illustration of the development of alloy design is given in [8]. At first, one matrix base element is used, striking examples are alloys based on copper or iron. The second element was added to improve certain properties of the main one. According to the reasoning of the authors [8], metal-matrix composites and intermetallic compounds began to develop more intensively from the 1970s of the last century. In the form of a matrix, traditional aluminium alloys were used, then alloys based on Ti–Al, Ni–Al, Fe–Al and others, and third and fourth elements were added to them. The use of rapid solidification technologies has led to the creation of alloys with many components. The principle of selection of elements to certain base elements for rapid solidification technologies was the selection of elements that contribute to the creation of a fine-grained structure, or contribute to the appearance of an amorphous phase. Having cited all the above considerations, the authors proposed a new concept of creating multicomponent alloys, the constituent elements of which are introduced into the alloy in equal molar fractions. It was expected that the alloys would be brittle due to the formation of many intermetallic compounds, but the result turned out to be different. The obtained compounds turned out to be more stable due to the large entropy of mixing. The theoretical basis for the creation of multicomponent alloys is Boltzmann's hypothesis about the relationship between the entropy of a system and the number of its possible microstates or the complexity of the system. The result of using this approach was the creation of high-entropy multicomponent alloys using the concept of configurational entropy. Examples of such alloys are given in work [8]. High-entropy alloys demonstrate [9] martensitic transformation and the ability to restore shape. In [7], the authors rightly noted that changes in the chemical composition and/or microstructure parameters (*i.e.*, parameters of thermomechanical processing and the alloy production method) affect the parameters of the martensitic transformation. The task of creating multicomponent alloys requires the creation of work in a multidimensional, nonlinear, highly singular mathematical space. Moreover, in such a space, it is necessary to carry out point studies, which is quite expensive. The authors [7] also analyse the change of the chemical component of the alloy design and come to the conclusion that by changing the 'chemistry' it is possible to achieve undesirable properties. They also analyse the use of combinatorial approaches, but find a drawback there, which consists in the complexity of processing the multidimensional and multielement space of multielement multifunctional alloys. They also indicate the complexity of first-principle calculations. In general, according to them, today's models allow analysing models for the creation of alloys only within the framework of some alloy systems. The surrogate model created by them will make it possible to make such a 'design' for many systems, while separately taking into account the weight of the chemical factor and factors of thermomechanical processing. Consider a surrogate CatBoost model for predicting recovery temperatures.

Selection of data: step 1 is the formation of data on chemical composition (the data of binary NiTi alloyed NiTi were used for the analysis, resolution of chemical composition 0.1 at.%; step 2 is taking into account the parameters of thermomechanical processing: heat treatment, rolling, extrusion; step 3 is the data processing: the results of both steps are entered into the list of primary parameters for ML of the surrogate model (actually, the result of the model was the phase transformation temperatures); step 4 is sifting out clearly unsuitable data and forming a 'reliable set'.

Training and Building a Strong Algorithm. As a result of the analysis, the authors established that the CatBoost model is optimal for ML, and the previous history of the ML algorithm, evolutionary methods, and Bayesian optimization hyper parameters were used. Thus, this model can be used to design alloys with given MT (martensitic transformation) parameters.

With the help of Shapley values, the importance of the influence of various factors of thermomechanical processing is taken into account. The authors of this paper really successfully predicted the phase transformation parameters for a number of nitinol-based alloys. Thus, ML is a promising direction for forecasting transformation parameters. However, there are a number of issues related to the optimal formation of the input data set, the creation of the error function, and other issues that are quite difficult. It is difficult to select data, since they must be taken from a large number of works, the authors of which studied various issues, and therefore there will be a difference in the methods of manufacturing alloys, types of thermomechanical processing, which will complicate the process of learning the model

In our work, we tried to simplify the forecasting process and simply process the existing data using a linear polynomial. Such work will allow us to see the simplest picture of alloy production and the creation of the necessary phase transformation parameters by changing the chemical composition and TMT parameters. The values of the coefficients of the polynomial will indicate the 'weight' of the TMT parameters and chemical composition.

2. EXPERIMENTAL DETAILS

Alloys for research were produced using arc melting in an argon atmosphere. The weight of the casting was 30 g, pure Ni, Ti components with a purity of 99.99% were used as filler materials. Analysis of the chemical composition after melting was carried out with the help of x-ray spectral analysis (x-ray fluorescence spectrometer VRA 20 method of x-ray analysis, ГОСТ 28033-89). After production, the alloys were examined in the cast state and after a series of thermomechanical treatments (TMT): 1) holding at 500°C for 5 hours and quenching in water at the temperature of 20°C; 2) hot rolling at the temperature of 900°C, then, holding at 500°C for 5 hours, and quenching in water at the temperature of 20°C. The parameters of the phase transformation were estimated by measuring the dependence between the deformation caused by the action of the external load and the change in temperature, and the load is carried out using the three-point bending technique [10]. This one was done in a similar way in works [10, 11].

3. RESULTS AND DISCUSSION

3.1. As-Cast Conditions

The first series of studies was carried out with samples in the cast state. Table 1 shows the results of determining the parameters of di-

TABLE 1. Values of characteristic transformation temperatures for the studied alloys in the as-cast state of the NiTi system.

Composition	Ni/Ti	M_s, °C	M_f, °C	A_s, °C	A_f, °C
$Ni_{50}Ti_{50}$	1	70	40	73	100
$Ni_{51}Ti_{49}$	1.04	−10	−90	−50	15
$Ni_{51.5}Ti_{49.5}$	1.06	−10	−160	−160	20
$Ni_{52}Ti_{48}$	1.083	−20	−150	−150	35

rect (martensitic) and reverse (austenitic) transformation in the cast state, and Fig. 2 shows the dependence between the temperature of the beginning of the direct transformation of M_s and the ratio between nickel and titanium $M_s = f(\text{Ni/Ti})$, where Ni/Ti is the ratio between nickel and titanium, M_s is temperature of the beginning of direct transformation, M_f is temperature of the end of direct transformation, A_s is temperature of the beginning of reverse transformation, A_f is temperature of the end of reverse transformation. The analysis of these data with the help of linear approximation led to the creation of equation (2), which, in our opinion, most likely has a linear character and reflects the melting process. In further consideration, we will try to confirm this assumption.

Analysing the data, we can suggest that in the as-cast state the polynomial has the following form:

$$y = -1085x + 1141.2. \quad (2)$$

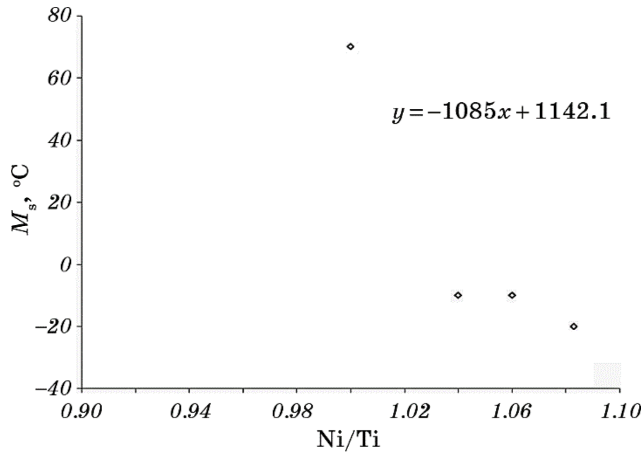

Fig. 2. Dependence between the temperature of the beginning of martensitic transformation (M_s) and the ratio between nickel and titanium (Ni/Ti): $M_s = f(\text{Ni/Ti})$. Samples in the as-cast state without TMT.

3.2. After Thermomechanical Treatment

Based on our results, taking into account thermomechanical processing, polynomials of the dependences between the Ni/Ti ratio and the temperature of the beginning of the martensitic transformation were constructed, taking into account TMT (Fig. 3). The following heat treatments were carried out hot rolling of as-cast samples from a temperature of 900°C.

The following dependence was obtained:

$$y = -1217.1x + 1248. \tag{3}$$

Exposure of as-cast samples at 500°C for 5 hours with subsequent quenching in water:

$$y = 240x - 242.45. \tag{4}$$

Another series of TMT consisted of a combination of rolling and heat treatment, namely, as-cast samples were rolled from 900°C, and then the rolled samples were kept for 5 hours at a temperature of 500°C, followed by quenching in water at room temperature (RT):

$$y = 465.6x - 474.4. \tag{5}$$

To simplify the analysis, we summarize all polynomials in Table 2.

The most complete overview of NiTi alloys is given in the paper [11],

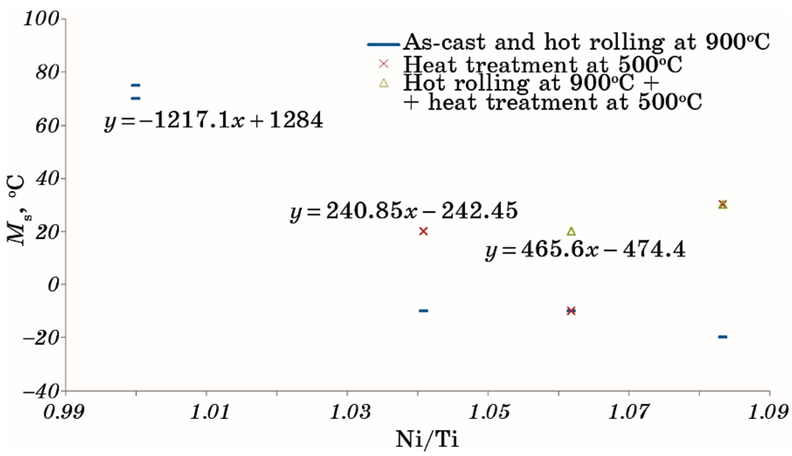

Fig. 3. Dependence between the temperature of the beginning of direct transformation (M_s) and the ratio between nickel and titanium (Ni/Ti): $M_s = f$(Ni/Ti). Samples after various thermal and thermomechanical treatments.

TABLE 2. Polynomials for the studied NiTi alloys after a series of thermomechanical and thermal treatments.

Thermomechanical or heat treatment	Connection polynomial	Reference
As cast condition	$y = -1085x + 1142.2$	
Rolling of as-cast samples from a temperature of 900°C	$y = -1217.1x + 1248$	
Exposure at 500°C for 5 hours with subsequent quenching in water	$y = 240x + 242.45$	
Rolling of cast samples from 900°C, rolled samples were kept for 5 hours at a temperature of 500°C, followed by quenching in room temperature water	$y = 465.6x - 474.4$	
Samples were hardened from 1000°C (linear part-on)	$y = -4088.6x + 4135.8$	Data for constructing the polynomial are taken from work [11]

and its authors used quenching from 1000°C in water at 20°C as heat treatment. Based on the data of this work, we also constructed a polynomial (6) of the dependence of the temperature of the beginning of the martensitic transformation on the ratio between Ni/Ti (the polynomial was constructed under the condition that the samples were quenched from 1000°C). It should be noted: if the polynomial is constructed according to all the data of the work [11], then, it is a polynomial of the second order (Fig. 4, Table 3):

$$y = -20031x^2 + 37891x - 17843. \quad (6)$$

As can be seen in Fig. 4, up to the ratio Ni/Ti ≈ 1, the temperature M_s almost does not change, when going from 1 to 1.07, the dependence $M_s = f(\text{Ni/Ti})$ is linear. Since our studies were conducted in the same 'linear range' and the data we obtained are described by a linear polynomial using the data of work [11] in the range 1 to 1.07, such a section can be described by a linear polynomial (Table 2):

$$y = -4088.6x + 4135.8. \quad (7)$$

Thus, it can be concluded that when constructing the approximate dependence of $M_s = f(\text{Ni/Ti})$ as a linear function:

$$y = kx + b; \quad (8)$$

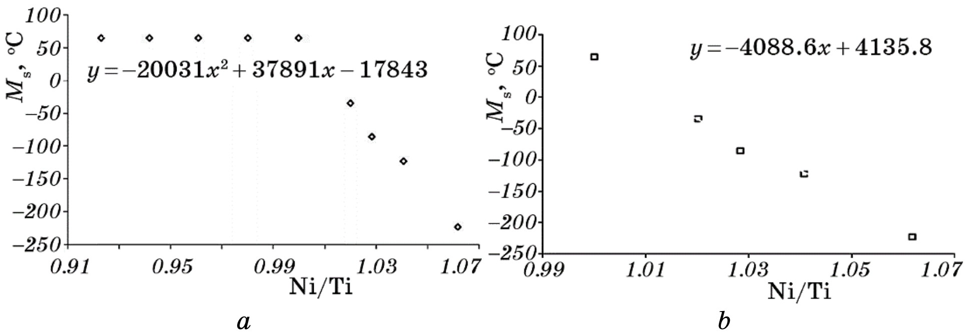

Fig. 4. The dependence between the temperature of the beginning of the direct transformation M_s and the ratio between nickel and titanium $M_s = f(\text{Ni/Ti})$ is constructed according to the data of [11]: entire ratio range Ni/Ti (*a*), only Ni/Ti = 0.99–1.07 (*b*).

in the latter, the coefficients *k* and *b* change depending on the previous history of the samples.

We also note that the coefficient *k* varies depending on the history of the sample's production. As can be seen from Tables 1 and 2, in the case of as-cast samples, $k = -1085$, and for hot rolled samples, changes it to −1217.1; hot rolled samples with additional annealing leads to a value of 465.6.

The conducted microstructural studies revealed a change in the microstructure after rolling in relation to the as-cast state (Fig. 5). A change in grain shape is observed in the rolled sample. The average grain size changes slightly from the order of 30–55 μm in the as-cast

TABLE 3. Polynomials for the NiTi system alloys studied in the entire range of the Ni/Ti ratio and only its linear part.

Thermomechanical or heat treatment	Connection polynomial	Reference
Not specified by the author traditional production method	$y = -29104x^2 + 56201x - 27047$, entire range	[15]
Not specified by the author traditional production method	$y = -3471.7x + 3534.3$, linear part	[15]
10 hours of annealing at 1050°C and quenching in water, 30 hours of annealing at 600°C and quenching in water Additive manufacturing method	$y = -3361.4x^2 + 6571.4x - 3145.2$, entire range $y = -761.26x + 848.55$, linear part	[16]
Quenching from 1000°C traditional production method	$y = -20031x^2 + 37891x - 17843$	[11]

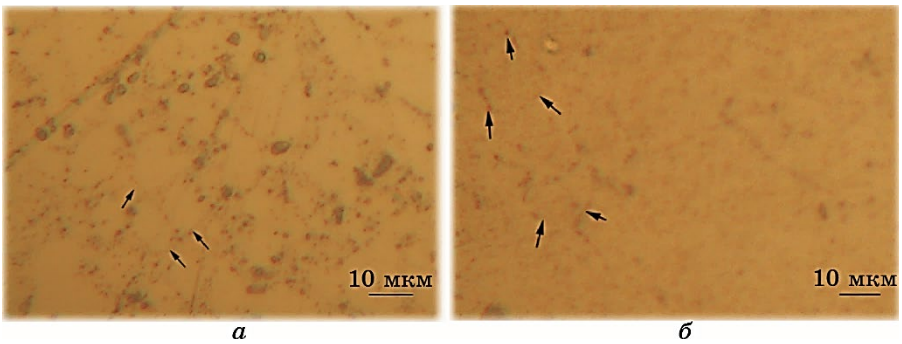

Fig. 5. Microstructure of as-cast alloy and after hot-rolling $Ni_{50}Ti_{50}$: in the as-cast state (*a*), after transverse hot-rolling (*b*).

state to the order of 25–35 μm after hot rolling, and there is an elongation of the grains in the rolling direction.

Therefore, it can be assumed that the change in the coefficient k is related to the change in the microstructure, and probably to the release of Ti_3Ni_4 particles due to the presence of the R phase, which is released during the annealing process, and the appearance of internal stresses that arise during the annealing process.

Let us consider the results of the authors of the work [12], where the alloy $Ti_{49.1}Ni_{50.9}$ was studied 1) in the as- cast state, 2) the samples in the as-cast state were subjected to hot rolling in the temperature range of 845–955°C, 3) the cast samples were rolled on hot and then subjected to a cold draft. It should be noted that the cast samples did not demonstrate the presence of texture, and the samples after hot deformation and cold deformation by broaching revealed the presence of texture in the direction of the deformation axis.

The authors of the work [12] pointed out another important application of nitinol castings of large sizes, namely as limiters of the movement of bridges, and such parts of bridges represent a massive casting after thermomechanical processing. Production of this casting consists of two parts: melting and heat treatment. The process of obtaining such a part of this production can be described with the help of our polynomial casting (2) and polynomial (5) a combination of rolling and thermomechanical processing. Let us consider them more carefully. Thus, the value of $k = -1085$, and $b = 1141.2$ in polynomial (2) describes ‘obtaining a cast state’, and after thermomechanical processing, these coefficients are $k = 465.6$, $b = -474.4$. Using both our results and the data of [12], it can be assumed that the change in the value of k and b reflects a change in the samples. Thus, according to our data, the appearance of texture was established, and this fact was also established in the work [12]. In addition, the release of Ti_3Ni_4 particles in the cast samples is random, and rolling and additional annealing led to the coherence of the release of these particles and the appearance of a texture, $M_s = 40°C$ after rolling and annealing and $M_s = 20°C$ in the as-cast state (although it is difficult to determine due to the blurring of the peak on the presented results of dynamic mechanical analysis) [12]. The closest to this is our $Ni_{51.5}Ti_{49.5}$ alloy, which showed similar properties; it can also be assumed that the separation of particles in our case is also coherent. When comparing the data, it should also be considered that the crystallization in the authors of this work took place in a crucible with cooling with a furnace, and in our work, the crystallization took place in a copper water-cooled basin, so the comparison of the data is somewhat complicated, although overall, they correspond to situations.

It was found that a polynomial of linear form allows describing both the process of melting and obtaining a casting as well as the process of thermomechanical processing. The scheme of 'polynomial operation' is shown in Fig. 6.

A comparison of all the above dependences shows that the change in the values of k and b testifies to the influence of the particle release processes in different TMT regimes. In addition, the influence of internal stresses arising from rolling, as well as the presence of the R phase, which is probably released during the annealing process, should be taken into account.

It is necessary to mention the methods of additive technology, which were mentioned above. With the help of three-dimensional printing, you can get an almost ready-made product, when hiring, such a general opinion exists in the world today. The work [13] gives eight general steps that are included in the stages of production of a part using additive technologies: 1) creation of a 3D CAD model of the product, 2) converting the model into STL format, 3) transfer of the file to the equipment, on which the detail will be created using the method of additive technology, 4) machine settings, 5) production, 6) opening the machine and removing the part, 7) treatment to which the part is subjected after producing.

The authors of this work analyse the possibilities offered by additive technology for obtaining finished nitinol products that demonstrate the ability to restore shape at specified temperatures and have arbitrary mechanical characteristics. The work [13] also states that meth-

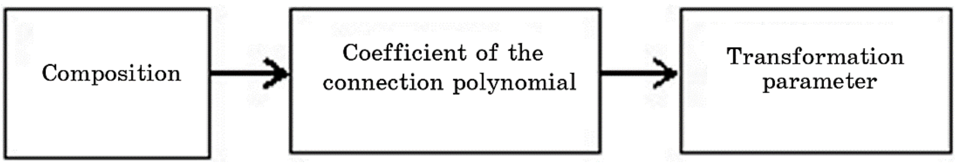

Fig. 6. Scheme of 'work of the black box'.

ods based on laser melting are quite attractive for use. There are two main approaches: a) electron-beam melting (EBM); b) laser-beam melting (LBM). The main difference in the methods is that photons are used in LB instead of electrons in EBM as energy sources for powder melting. It is difficult to say which of the methods is more suitable, since they are quite similar in result. In work [14], a $Ni_{50.2}Ti_{49.8}$ test sample was studied, which turned out to be suitable for creating actuator. This sample demonstrated the presence of the shape-recovery effect and good functional properties.

Disadvantages include a lower fracture strain than a sample obtained by the traditional method. Moreover, the authors used binary nitinol powder for production. The authors of this work note that the production of NiTi is a rather complex process due to the high reactivity of the alloy and the formation of impurities enriched in oxygen Ti_2Ni and TiC.

Photographs of the microstructure of the alloy given in [14] show that it has the character of longitudinally applied layers. In a certain sense, the microstructure of nitinol in the VIM produced by the traditional method (Fig. 5, *a*) or VIM has grains conventionally, looking like ‘balls’, while the microstructure of the ‘printed’ material looks like ‘bricks’ [14] , which have quite significant longitudinal dimensions (about 250 μm) and much smaller transverse ones (50–100 μm). Of course, these are very approximate estimates.

The authors of the work [15] believe that minimal changes in the chemical composition of nitinol create a significant impact on the properties. We slightly changed the data given by them by replacing the Ni content in the temperature dependence of M_s with the ratio between Ni and Ti. In Figure 7, it can be seen that when the ratio between Ni and Ti is of the order of 1, the dependence changes approximately to 1, the M_s temperature is practically independent of the ratio between

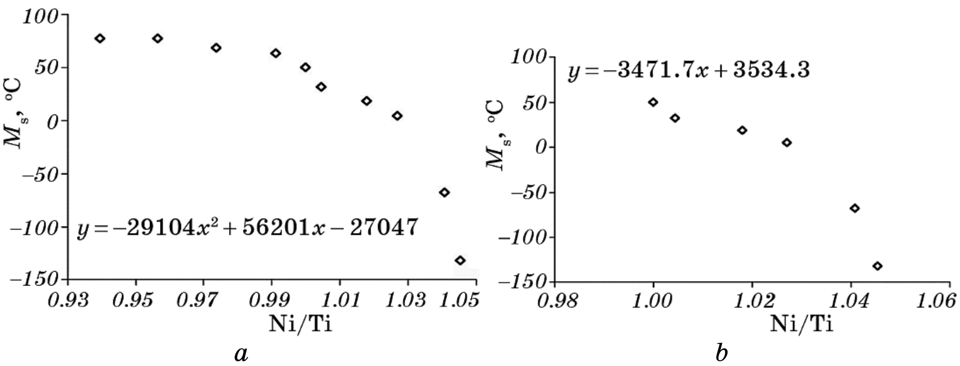

Fig. 7. Dependence between the temperature of the beginning of the direct transformation and the ratio between Ni/Ti [15]: the entire range of the Ni/Ti ratio (*a*), only Ni/Ti = 1–1.05 (*b*).

Ni and Ti and has an almost constant character (Fig. 7, *a*), and when Ni/Ti = 1–1.05, a fairly close to linear dependence is observed.

The authors of this work used nitinol powder from a pre-made casting as a material for printing. After the production of the samples, the following heat treatment was applied, annealing at 850°C for 15 minutes, followed by quenching in water. Then, in order to increase the temperature at the end of the reverse transformation, heat treatment was carried out at 350°C and 450°C for an hour, followed by quenching in water.

The authors believe that thermomechanical treatment allows controlling the transformation temperatures, the size of the powders affects the final concentration of oxygen in the powders and thus the transformation temperatures.

In work [16], the authors created 3*D* samples using the so-called (LENS = formation of a mesh using a laser) laser mesh method. In their work, the authors created a large number of samples from 48 at.% NiTi to 51.6 at.% NiTi.

In this work ([16] in Fig. 4), the dependence of the characteristic transformation temperatures on the Ni content is shown, we slightly changed the form of the dependence and created the dependence of the M_s temperature on the change in the ratio between Ni and Ti (Fig. 8).

It should be noted that the authors of [16] printed the samples, and Ni powders and Ti powders were first mixed, and then they were exposed to the laser beam. Powders of pure elements served as raw materials in this case, while in previous works powders obtained from binary NiTi were used. The obtained samples were subjected to homogenizing annealing at 1050°C for 10 hours followed by quenching in water. After that, the samples were again kept at 650°C for 30 hours and quenched in water, and such heat treatment was required to lower the phase transformation temperature by forming the Ti_3Ni_4 phase. Ana-

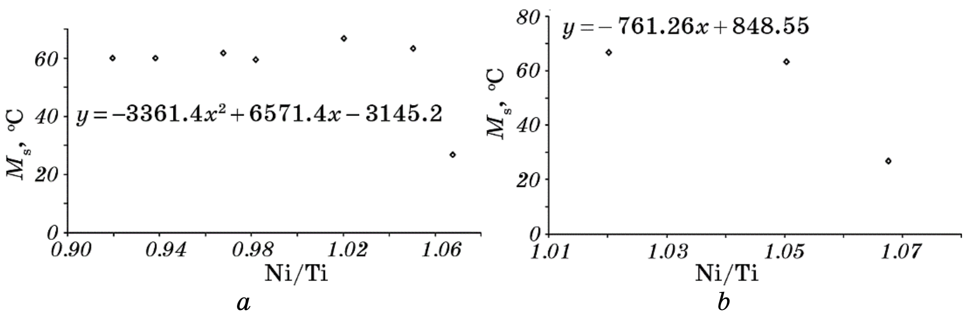

Fig. 8. Dependence between the temperature of the beginning of the direct transformation M_s and the Ni/Ti ratio $M_s = f$(Ni/Ti) [16]: the entire Ni/Ti ratio range (*a*), only Ni/Ti = 1.01–1.07 (*b*).

lysing Figure 8, it can be said that the dependence $M_s = f(\text{Ni/Ti})$ behaves in the same way as for samples obtained by the traditional method, that is, up to the ratio Ni/Ti ≈ 1, the temperature of M_s can be considered conditionally constant, and after a linear section of temperature decrease is observed.

With the help of 'Excel' capabilities, we built a description of the data dependencies of the entire range of ratios with a second-order polynomial and separately for the linear part with an ordinary linear polynomial (Fig. 7). An examination of Fig. 7 shows that the behaviour of alloys obtained by additive methods is similar to alloys obtained by traditional methods.

In work [3], a review of works devoted to NiTi with shape memory obtained using additive methods was carried out. They believe that selective laser methods are promising for obtaining ready-made parts at once, especially parts of complex shape. They found that during the application of such methods for the manufacture of samples, evaporation of Ni is observed, which contributes to the formation of secondary phases containing Ni in their composition, and therefore changes the composition of the matrix and the temperature of the phase transformation. Conducting heat treatment after the additive method of obtaining does not completely solve this problem. It needs additional research. The use of polynomials to describe the production process and subsequent heat treatment is one of the ways to overcome such a shortcoming, since the analysis of polynomials will allow us to get closer to their optimal coefficients and, thus, adjust the parameters of technological processes.

In our work, alloys were studied in the cast state and the dependence $M_s = f(\text{Ni/Ti})$ was constructed (Table 1, Fig. 1), and the same alloys were studied after thermomechanical treatments (Table 2, Fig. 3). The analysis of these dependences allows us to note that an increase in the Ni/Ti ratio lowers the temperature of the beginning of the transformation, and the dependence $M_s = f(\text{Ni/Ti})$ is close to linear in nature, so a linear polynomial (2) was used for the description. We carried out the deviation of the chemical composition of the alloy from the specified (that is, what we wanted to get) using the x-ray fluorescence analysis method.

The casting was cut along the edges and samples were taken for analysis from two opposite extreme points of the casting, after which the average value was calculated, which was considered the real chemical composition. Our data indicate that, in this series of alloys, we lost Ti, and the maximum error in determining the chemical composition reached 0.57% wt. When analysing the error, all possible sources of its occurrence are taken into account, namely, error when weighing the charge, operator error, error in determining the chemical composition, and others. When determining the chemical composition, we determined the average value and operated with it as a real composition, although there is usually a certain dispersion of the chemical composition on the casting. It is difficult to compare such data, because the authors of other works do not fully cover this issue.

Analysis of Table 3 and Figs. 4, 7, 8 allows us to do the following considerations. Practically, consideration of the entire range of the ratio between Ni and Ti allows us to single out a certain point where Ni/Ti $\approx$ 1, which is characterized by a break and the beginning of the linear dependence $M_s = f$(Ni/Ti) for both traditional and additive production methods. The question to which there is no answer yet is which polynomial is better to use to describe the process in the 'black box': power polynomial of at least the second order, which allows working in the entire range of compositions where MT occurs, or linear, which describes the data in the range interesting for production. As said above, when using ML methods, the authors [7] managed to predict the temperatures of phase transformations in a wide range of alloys using the surrogate CatBoost model using ML, taking into account the chemical composition and parameters of TMT. However, it is not entirely clear from this work what data the authors used, although this does not diminish the importance of the results of the work: the authors managed to predict the parameters of the transformation taking into account the chemical composition and TMT. This approach is quite complex and the question arises as to how much it can be applied in real production. We offer a simpler way of describing the production process using a linear polynomial in the range of Ni/Ti ratios $\approx$ 1. It should be added that our approach could be applied when training algorithms in order to create strong algorithms in ML.

4. CONCLUSION

Based on our own research, a 'black box' model was proposed, with the help of which we obtained an empirical law of change in the temperature of the beginning of the martensitic transformation (M_s) from a change in the ratio between the Ni/Ti components in the form of a linear polynomial: $y = kx + b$. It is shown that when constructing the approximate dependence $M_s = f$(Ni/Ti) as a linear function, the coefficients k and b change depending on the previous history of the samples.

The analysis of literature data and the results obtained by us allows us to identify an inflection point in the dependence of $M_s = f$(Ni/Ti), which is located in the vicinity of the ratio Ni/Ti $\approx$ 1.

The temperature of MT does not change in the Ni/Ti $\approx$ 0.9–1 dependence interval and decreases linearly, when Ni/Ti $\approx$ 1–1.07.

The analysis of literature data showed the similarity of the behaviour of the function $M_s = f$(Ni/Ti) for alloys obtained by traditional methods and additive methods.

The polynomials proposed in the paper can be used for the purpose of creating a strong machine-learning algorithm, and for adjusting the processes of manufacturing and thermomechanical processing of alloys.

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