3. MODELLING OF PROCESSES OF THERMOPLASTIC PROCESSING OF INTERMETALLIC ALLOYS UNDER NON-STATIONARY TEMPERATURE CONDITIONS

Light alloys, based on titanium aluminide with *TiAl* phase, are currently considered as potential construction materials to use at temperature range 600–900 °C and they, as supposed, will find wide application in the near future. It has a unique complex of mechanical properties in comparison with traditional construction materials. It includes high specific strength and elasticity, which persist to high temperatures, high heat and oxidation resistance. These properties are due to the highly directional covalent component in the interatomic bond and the ordered atomic structure. At the same time, *TiAl* alloys are predominant in comparison with ceramic materials, owing to definite ductility and fracture toughness. The most promising application of *TiAl* alloys is in aircraft and space vehicles. The lightweight exterior panels with cellular filler and rigid thin-walled integral structures can be manufactured from these materials [40].

The main attention of the intermetallic γ-*TiAl* alloys developers in the last two decades was concentrated on achieving the optimal combination of mechanical properties by varying the microstructure from fully lamellar to duplex with varying grain size and plate thickness [41]. Depending on the alumina content alloys, based on γ-*TiAl* are divided into two groups: single-phase γ-alloys (50–52 % *Al*) and two-phase $\gamma + \alpha_2$ alloys (44–49 % *Al*). Through the obtaining technology with hot-deformation modes and heat treatment of biphasic alloys, three basic types of intermetallic structure are distinguished: lamellar, recrystallized (globular) and bimodal (duplex). Nowadays,

three generations of industrial intermetallic alloys, based on γ-*TiAl* with different types of structure, are developed [42].

In our opinion, to give the *TiAl* alloy product the final properties, it is necessary to subject plastic deformation in the high-temperature phase region to obtain a plate structure. It provides the best combination of high-temperature properties – strength, creep resistance, with room ones – plasticity and fracture toughness. Apparently, plastic deformation can be effective not only for the production of fine-grained semi-finished products but also for controlling the parameters of the plate structure in *TiAl* alloys. In particular, it can be used for obtaining plate-like microstructures with a small colony size and nanocrystalline interplanar spacing, which are of great interest [43].

The purpose of this work is to investigate the nanostructure formation in intermetalide γ-*TiAl* alloys by using a complex plastic deformation technology under non-stationary temperature conditions with niobium doping. Also in given work, the using of Hall-Patch model, the interrelation of the nanostructured quantities with strength characteristics is considered. It allows to obtain materials with increased plasticity by an optimal combination of mechanical properties over a wide range of temperatures.

3.1. Modelling of deformation and rheological parameters for the production of intermetallic alloys under conditions of thermoplastic treatment

Based on the results of works [44–46] and previous independent studies of the thermochemical pressing process (TCP process) [7, 8], an attempt was made to determine the main patterns of deformation and structure formation, to determine the ways and methods of controlling the processes of forming the structure and properties of pressed products. To solve the problem, the method of mathematical

modeling was used, during the implementation of which the following main stages can be conventionally distinguished: idealization of the internal properties of the given process (object) and external influences (building a physical model); mathematical formulation of the behavior of a physical model (construction of a mathematical model); choosing a method for researching a mathematical model and conducting this research; analysis of the obtained mathematical result.

In the mathematical description of TCP-process it is necessary to take into account the thermokinetic characteristics of the process, the velocity of the reactant and its macroscopic density. Therefore, in addition to the kinetic equations for the formation of the intermetallic structure, the activation energy and chemical transformation, it is necessary to use the rheological equations used in describing the rheological models, which allows us to carry out numerical calculations of the kinetic dependences of the basic parameters of the process of compressing the product of high-temperature synthesis – the temperature of synthesis, the completeness of chemical transformation, macroscopic the density of the product of synthesis, the level of elastic stresses in the product, the velocity of its melting point static deformation and grain size finite product.

The starting material for SHS synthesis of the intermetallic compound *TiAl* is a powder mixture of nickel with aluminum, placed in the form of a molding in a closed mold. The powder compactor is warmed up to a given temperature and ignites in the mode of thermal explosion when the external pressure is applied, under the action of which the compression deforms. The plastic deformation ceases when the synthesis product is cooled to a temperature T_k, at which it loses ductility.

For a mathematical description of the process of extrusion of a high-temperature synthesis product, it is necessary to determine a system of equations that takes into account the distribution of the thermo-kinetic and rheological properties of the synthesis product in a mold and caliber. Assuming that the extrusion occurs in conditions

of one-sided compression of the synthesis product in the absence of friction on the walls of the mold, we can write the initial equations:

1. Equation of continuity [49]:

$$\frac{\partial(\rho\rho_1)}{\partial t}+\frac{\partial(\rho\rho_1 V)}{\partial z}=0. \tag{3.1}$$

2. Equation of motion [9]:

$$\rho\rho_1\left(\frac{\partial V}{\partial t}+V\frac{\partial V}{\partial z}\right)=\frac{\partial\sigma_{zz}}{\partial z}, \tag{3.2}$$

with rheological correlations:

$$\sigma_{zz}=\left(\frac{4}{3}\mu+\xi\right)\frac{\partial V}{\partial z}, \tag{3.3}$$

$$\sigma_{rr}=\sigma_{\theta\theta}=\left(-\frac{2}{3}\mu+\xi\right)\frac{\partial V}{\partial z}, \tag{3.4}$$

where ρ – relative density, ρ_1 – density of the condensed phase, t – time, V – viscous flow velocity, z – axial coordinate, σ_{rr}, $\sigma_{\theta\theta}$, σ_{zz} – radial, tangential and axial stresses, μ, ξ – shear and bulk viscosity.

It is assumed that the distribution of relative density in the initial powder mixture is uniform: $\rho(z,0)=\rho_0$.

In the case where the density of the product SHS differs from the density of the original powder mixture:

$$\rho_1=\frac{\rho_c\rho_f}{\alpha\rho_c+(1-\alpha)\rho_f},$$

where ρ_c – initial density of the mixture:

$$\rho_c=\frac{\rho_{Ti}\rho_{Al}}{\rho_{Ti}(1-c_0)+\rho_{Al}c_0},$$

where ρ_{Al} – aluminum density; ρ_{Ti} – titanium density; ρ_f – the density of the reaction product; α – depth of chemical transformation of the intermetallic compound during the synthesis; c_0 – relative mass concentration of titanium in the initial binary powder mixture.

The depth of chemical transformation is defined as:

$$\frac{d\alpha}{dt} = f(\alpha) k_o \exp\left(-\frac{E}{RT}\right),$$

where $f(\alpha)$ – kinetic law; k_0 – pre-exponential factor; E – activation energy of a chemical reaction.

To determine the conversion depth (α), the Johnson-Mel-Avrami-Kolmogorov model was used to estimate the kinetics of the formation of new phases and structural components. This model assumes that the appearance of a new phase occurs uniformly throughout the volume, the rate of appearance of a new phase does not depend on its already available quantity [54, 55]. The equation is written in the form:

$$\alpha(t) = 1 - \exp\left(-Kt^n\right),$$

where K – is determined by the rate of growth of the phase in the volume and depends on the temperature and properties of the particular substance, n – parameter determined by the growth pattern of crystallites.

Different values of n correspond to different conditions for the formation and growth of embryos. If the cores are pre-formed and, therefore, they are all present from the very beginning, the transformation occurs only because of the 3-dimensional growth of the nuclei, then n is 3.

The parameter of crystallite growth rate K can be represented in the form:

$$K(T) \sim \exp\left(-E_a / RT\right),$$

since the crystallization process is thermally activated.

The dependence of the shear and bulk viscosity of the synthesis product on its density is of the form [49]:

$$\mu(\rho) = \mu_1 \rho^m, \ \xi(\rho) = \frac{4}{3}\mu(\rho)\frac{\rho}{1-\rho}, \tag{3.5}$$

where $\mu_1 = \mu_0 \exp(U/RT)$ – the viscosity of the non-flaking material basis, μ_0, U – physical constants, R – universal gas constant, T – temperature of the mixture, m – degree indicator.

3. Equation of thermal conductivity [46]:

$$c_1\rho\rho_1\left[\frac{\partial(\rho T_i)}{\partial t}+\frac{\partial(\rho V T_i)}{\partial z}\right]= \\ =\frac{\partial}{\partial z}\left[\lambda(p)\frac{\partial T_i}{\partial z}\right]+\rho\rho_1 Q\frac{\partial\alpha}{\partial t}-\frac{2\chi_i}{r_i}(T_i-T_0), \tag{3.6}$$

where T_i – the material temperature in the matrix ($i=1$) and in the caliber ($i=2$), $\lambda(\rho)$ – dependence on the density of the heat conductivity of the material, χ_i – effective heat transfer coefficient, r_i – radius of the cross section of the matrix and the caliber, $c_1=(1-\alpha)c_s+\alpha c_{TiAl}$ – heat capacity of the condensed phase; $c_s=c_{Ti}c_0+c_{Al}(1-c_0)$ – heat capacity of the initial mixture, Q – thermal effect of intermetallide formation reaction TiAl, T_0 – initial temperature.

The following assumptions were made to describe the process of compression of an intermetallic synthesis product in the mode of thermal explosion:

– the heating and cooling of the reacting powder system in the working space of the mold proceeds without a temperature gradient;

– the synthesis product is deformed in a homogeneous-stressed state;

– the heat sink from the mold can be neglected;

– the voltage at the upper boundary of the original powder compression in absolute value is equal to the compression force.

Thus, using the equation (3.1) and the relation (3.2), (3.3), the change in the density of the reactive in the mold of the powder system can be written as [10]:

$$\frac{\partial(\rho\rho_1)}{\partial t}=\frac{\rho\rho_1 N}{4/3\mu+\xi}, \tag{3.7}$$

where N – the value of the applied pressure.

A equation of the thermal balance of a synthesis product, taking into account a number of assumptions, can take this form [50]:

$$c_1\rho\rho_1\frac{\partial T}{\partial t}=\rho\rho_1 Q_{TiAl}\frac{\partial\alpha}{\partial t}-\chi_1\frac{S}{V}\left(T-T_0\right), \tag{3.8}$$

where S – total area of the inner surface of the mold, V – volume of molds.

The equations (3.7) and (3.8) allow us to quantify the parameters of the process of TCP pressing of the intermetallic compound synthesized under pressure. The process of forming a structure in a synthesized product under pressure is considered in the assumption that the initial grain size corresponds to the size of the initial particles of the refractory component (titanium), i.e. D0 = D_{Ti} (D_{Ti} – the diameter of the titanium particle).

The kinetics of grain growth as a result of the recrystallization of the synthesized intermetallic product is estimated from the equation [49]:

$$\frac{\partial D}{\partial t}=\frac{K\left(T_1\right)}{D^h}, \tag{3.9}$$

where D – the initial size (diameter) of the grain, $K=k_0\exp\left(-E_a/RT\right)$ – depends on the constant temperature, k_0 – pre-exponential factor, E_a – energy of activation of grain growth, h – degree of magnitude close to 1.

The amount of deformation of the synthesized product during extrusion is determined from the equation:

$$\varepsilon\frac{r_1^2-r_2^2}{r_1^2}. \tag{3.10}$$

Dependence of the grain size of the synthesized product on the degree of its deformation during extrusion is described by the empirical relations [51]:

$$D_\varepsilon = \frac{D}{\sqrt[3]{A\left(\frac{\varepsilon}{\varepsilon_{кр}}\right)^2}}, \qquad (3.11)$$

where $\varepsilon_{кр}$ – the degree of deformation at which the formation of the nucleation of recrystallization occurs ($\varepsilon_{кр} \approx 0{,}1$), A – coefficient of form of intersection of the initial grain ($4\pi / 3 < A < 6$).

A quantitative estimate of the grain size in the intermetallic product of the synthesis after extrusion can be carried out using the heat balance equation (3.7) and having carried out the derivative in time (3.8) in the derivative in the temperature.

Thus, after carrying out the necessary transformations, for the final grain size of the intermetallic product under the TCP compression, we can write [52]:

$$D_k = \sqrt{D_\varepsilon^2 + \frac{c\rho_0\rho_c r_2 R T_{a\partial}^2}{\chi_2 E_a \left(T_{a\partial} - T_0\right)} k_0 \exp\left(-\frac{E}{RT_{a\partial}}\right)}. \qquad (3.12)$$

From equation (3.12) it is evident that the final grain size in the TCP-process product depends on the size of the grain of the product synthesized in the mold, the degree of deformation of the synthesized product during extrusion through the caliber, the adiabatic temperature of the synthesis of the extruded product and the speed of its cooling (depending on the temperature of the press shape, radius of its cross-section and coefficient of heat transfer of the synthesized product with the walls of the mold).

3.2. Numerical analysis of the influence of technological parameters on the structure formation processes

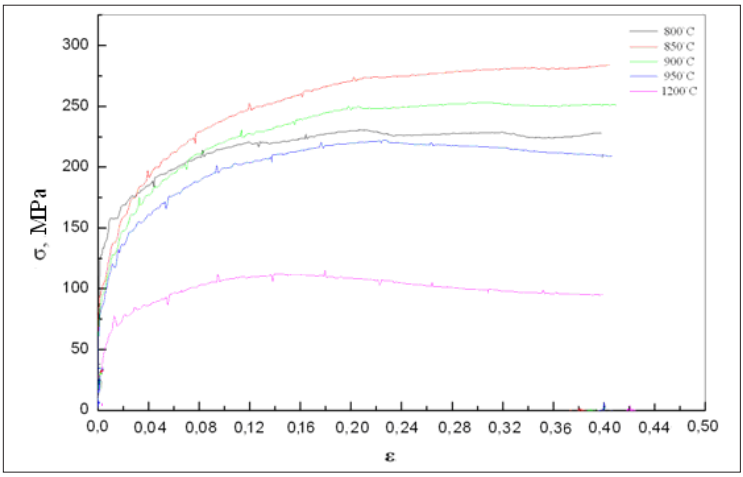
Computer simulation of the hot-deformation processes of intermetallic γ-*TiAl* alloys is made using the software package *Deform*. The *Deform* program is a powerful system for modeling technological processes designed to analyze the three-dimensional behavior of the metal under various pressure processing processes. The program is based on the finite element method, one of the most well-known, reliable and currently used calculation methods. An automatic grid generator allows you to build an optimized finite element grid, thickening it in the most critical areas. In addition, the program provides important information on material flow and temperature distribution during the deformation process, which allows modeling a complete list of pressure processing processes and solving deformation and heat transfer problems. In solving the thermal deformation problem of compressing γ-*TiAl* alloys into the *Deform* program, the following output data were integrated:

$H_0 = 50$ mm, $r_1 = 25$ mm, $r_2 = 15$ mm, T_{a0} (*TiAl*) 1654 K, $T_0 = 300$ K, $\rho_0 = 0.6$, $\rho_{Ti} = 4540$ kg/m^3, $\rho_{Al} = 2700$ kg/m^3, $\mu = 0.14$, $\rho_{TiAl} = 3800$ kg/m^3, $c_{Ti} = 540$ J/kg·K, $c_{Al} = 929.5$ J/kg·K, $c_{TiAl} = 600$ J/kg·K, $Q_{TiAl} = 8.1 \cdot 10^3$ kJ/kg, E_a(*TiAl*) = 79 kJ/mol, $D_{Ti} = 100$ μm.

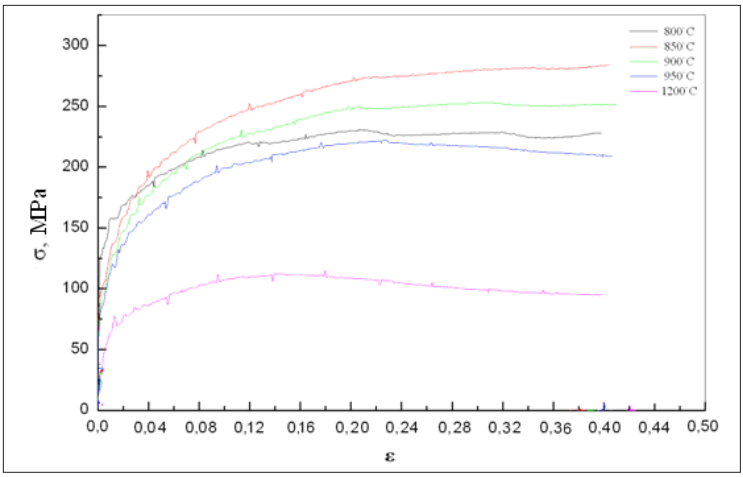
In work [52], based on experimental research's methods of kinetic interaction in intermetallic alloys in TCP conditions, it was established that for obtaining γ-*TiAl* alloy the activation energy was nearly 79 kJ/mole and pre-exponential coefficient $k_0 = 7.2 \cdot 10^8$ s^{-1}.

In solving the thermoformation problem of compressing γ-*TiAl* alloys into the Deform program, the following data were integrated:

– the rheological properties of the γ-*TiAl* alloys $\sigma = f(\varepsilon, u, T)$, obtained experimentally on the Gleeble-3800 complex (**Fig. 3.1**) [53], which makes it possible to carry out numerical calculations of the kinetic dependences of the basic parameters of the process



a



b

Fig. 3.1. Results of physical modeling of thermo-deformation treatment of the γ-*TiAl* alloy on the Gleeble-3800 complex: a is the strain rate, $a - u = 0.1\ s^{-1}$, $b - u = 1\ s^{-1}$

of compression of the product of high-temperature synthesis – the temperature of the system, the completeness of the chemical transformation, the macroscopic density of the synthesis product, the level of elastic stresses in the product, the speed of its plastic deformation and the grain size of the final product;

– parameters of the hydraulic press, according to the passport and the layout of the equipment;

– deformation and velocity (degree of deformation, displacement of the punch, etc.);

– temperature and temporal (thermophysical characteristics of the deformable and material of the technological instrument, coefficients of heat transfer, radiation, duration of pause, etc.).

To simulate the compression of the γ-*TiAl* alloy, the original finite element grid consisted of 100 elements grouped in a rectangle of 10 elements on one side. The sample in question was a cylinder 60 mm in diameter and 90 mm high.

The simulation results of the stress-strain state of *TiAl* alloys are presented in **Fig. 3.2**.

The process of extrusion is characterized by a stress of comprehensive compression, which provides the material the best in these conditions plastic properties. Under the influence of compressive stresses, the material flows in the direction of the largest gradient of stresses – from the surface of the punch, where they have the maximum value, to the caliber of the matrix (Fig. 3.2, *b*), where the normal stresses on the free surface of the tangent material are zero.

Comprehensive uneven compression provides the material with the highest ductility compared to other processes of metal treatment, but this feature of the process is manifested in extremely uneven deformations. In this case, only the compressive voltages acting continuously in the direction of extrusion from the maximum values to zero are not always in full volume of the deformed material.

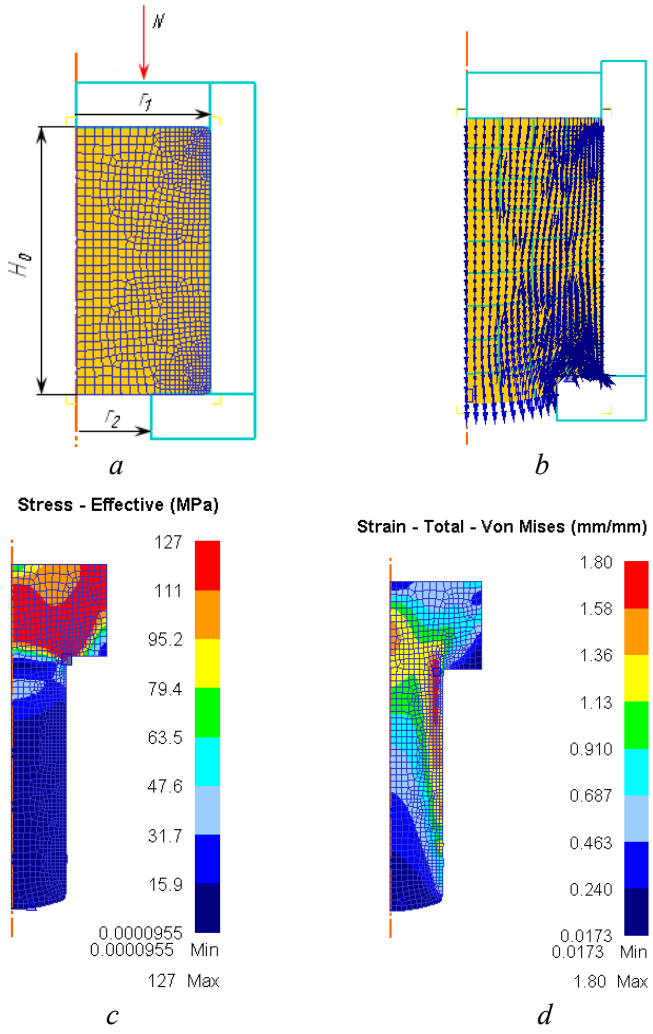


Fig. 3.2. Simulation of the process of TCP-process of the intermetallic *TiAl* alloy in the program Deform: *a* – the initial workpiece for calculation, *b* – the direction of the tensile metal in the workpiece, *c* – the pattern of the intensity distribution of stresses, *d* – the intensity of deformation

The presence of the difference between the intersections of the container and the caliber of the matrix, the forces of contact friction and other factors leads to the fact that the particles of the material begin to move not only in the directions of the greatest deformation, but also in transverse directions. The latter contributes to the emergence of local (additional) stresses, the magnitude of different, direction and sign, and the emergence of tensile stresses. This is facilitated by the movement of material particles along trajectories of different lengths with velocity, change in the process of passage through different zones. The results of modeling the stress-strain state of *TiAl* alloys are shown in **Fig. 3.3**.

In the conditions of the synchronization of thermal processes of the TCP and the dynamic compactation of the synthesis product, it is possible to obtain a compact intermetallic alloy with a highly dispersed structure, the size of which is much smaller than that of the

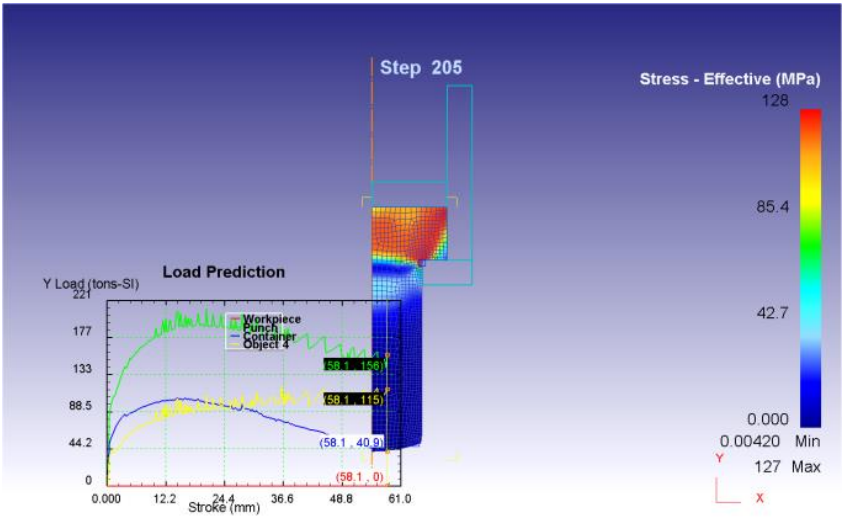


Fig. 3.3. Modeling of pressing processes of *TiAl* alloys

alloys obtained by the methods of casting, sintering or shock-wave action on the synthesized product. Grinding of grain of intermetallic alloy in the process of its synthesis under pressure occurs as a result of plastic deformation of the product of synthesis and high cooling rates (**Fig. 3.4**). High-temperature synthesis of the intermetallic compound γ-*TiAl* in a powder mixture of pure elements in the conditions of TCP-process at a thermal explosion at a minimum external pressure on the mixture allows obtaining an intermetallic synthesis product with an average grain size of ~ 30 μm.

An increase in the degree of plastic deformation of the intermetallic product synthesized under pressure in the conditions of the TCP-process allows to reduce the size of the grain in the final product by an order of magnitude and even to form a sub-microcrystalline granular structure in the intermetallic alloy. The graphical interpretation of calculated results is shown on Fig. 3.4.

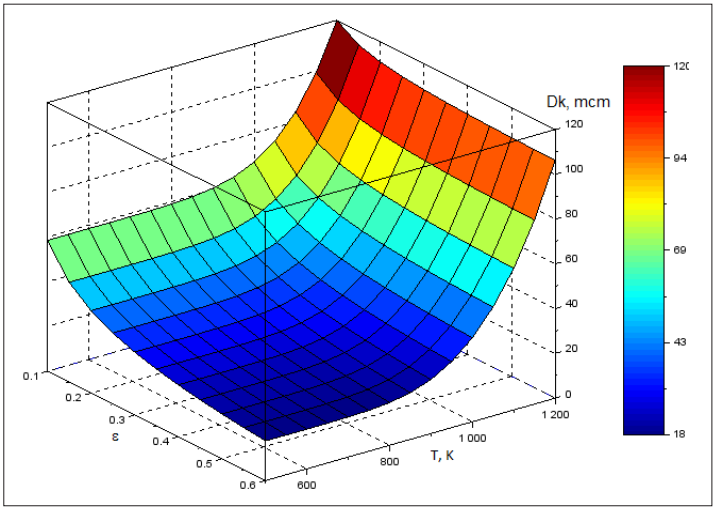


Fig. 3.4. The dependence of grain size of *TiAl* intermetallide on deformation and temperature degree

Thus, a mathematical model aimed at obtaining γ-*TiAl* alloys with a given structure and properties is proposed and implemented, based on the use of data on the features of the physical modeling of the TCP-process process and the DEFORM software complex. High-temperature synthesis of intermetallic compound γ-*TiAl* in a powder mixture of pure elements in the conditions of TCP-process allows to obtain an intermetallic alloy with an average grain size of ~ 30 microns.

The experimental compacting curves and the results of modeling the pressing of *TiAl* alloys allow us to fix four clearly defined zones that determine the staging of the structure formation in TCP-process (**Fig. 3.5**).

The first stage of pressing – from the bulk density (the characteristic of the initial material) to the density of the pore level, is characterized mainly by structural deformation, particle re-packing, change in pore space. The consolidation of the powder mixture occurs due to a decrease in the volume of air inclusions in the material and the closure of macropores.

The second stage, the stage of thermal autoignition, shows an abrupt increase in the relative density, which indicates a certain

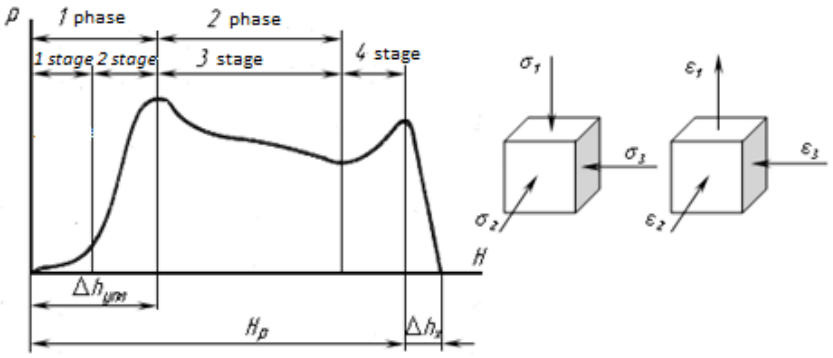


Fig. 3.5. Mechanical deformation scheme and loading schedule of TCP-process

self-tightening of the γ-*TiAl* alloy during the synthesis, apparently under the action of surface tension forces. The initial stage of the formation of titanium aluminide occurs.

The third stage – compaction is characterized by structural deformation. The threshold density of the stage is 83…95 %. In a system containing 39.6 wt% *Al*, the layer previously formed limits the movement of aluminum atoms to the titanium material. At the same time, the $TiAl_3$ layer builds up, which leads to an abnormal aluminum mass and the subsequent formation of titanium monoaluminide.

The fourth stage – the final stage of the structure formation will be the alignment of the composition of the intermetallic layers, primarily due to the recrystallization of $TiAl_3$ in *TiAl* and the secondary structure formation of Ti_3Al as a result of dissolution of the inner titanium core. In the last stage of compaction, the compact density reaches 98…99 % of theoretical density. The residual porosity of the intermetallic compound is 1…2 %.

Thus, preliminary research method aimed at obtaining γ-*TiAl* alloys with a given structure and properties based on the use of data on the physical modeling of thermal deformation processing on the Gleeble 3800 complex and the DEFORM software is proposed and implemented.

3.3. Effect of hot deformation on the structure formation and properties of intermetallic alloys

The investigated materials include elemental powders of 99.8 % pure titanium with an average particle size of 100 μm, 99.6 % pure aluminum with an average particle size of 70 μm and 99.8 % pure niobium with an average particle size of 100 μm. The powders were preliminarily mixed at a stoichiometric ratio for two systems in a Uniball 5 mill using any balls:

Ti-Al: Ti – 48 %, *Al* – 52 %;

Ti-Al-Nb: Ti – 42 %, *Al* – 50 %, *Nb* – 8 %.

The obtained mixture was compressed in a mold on hydraulic press with pressure of 300 MPa. The combustion process was carried out in the special furnace with protective atmosphere under normal conditions. The compaction of the synthesized samples was carried out at pressure of 100 MPa.

To evaluate the microstructure properties of the intermetallic compound, the rectangular parallelepiped samples were cut by size 5 mm × 10 mm × 10 mm.

The microstructure of the obtained alloys was researched with scanning electron microscope SUPRA 40 WDS.

To calculate limit stress of obtained alloys the Hall-Patch model was used [55–57].

The scientific novelty of the work is that the high-temperature synthesis of the intermetallic compound γ-*TiAl* in a powder mixture of pure elements, under the conditions of the TCP-process, at a thermal explosion at a minimum external pressure on the mixture allows to obtain intermetallic synthesis product with an average grain size of 30 μm.

Based on the results of our earlier works, related with TCP-process [54–55], it is necessary to establish the basic laws of deformation and structure of intermetallic alloys with unsteady temperature conditions.

The analysis of calculations has shown that in conditions of synchronized thermal SHS processes and dynamic compaction product synthesis, it is possible to obtain a compact intermetallic alloy of fine structure, which has grain size that much less than the alloys, obtained by casting, sintering or shock-wave action. It is found that high-temperature synthesis of intermetallic alloy *TiAl* powder in a mixture of pure elements in terms of TCP-process with thermal explosion provides a synthesis of intermetallic product with an average grain size ~30 microns. The increasing of plastic deformation degree will significantly reduce the grain size in the final product and more over will form intermetallic alloy with sub-microcrystal granular structure.

The fine-grained two-phase duplex structure of alloys has the best plasticity but at the same time, another not less important characteristic – the viscosity of the alloy is reduced. The optimum option is to obtain alloys with a fully lamellar two-phase (γ/α_2) structure with a certain amount of γ- and α_2-phases in the alloy (**Fig. 3.6**).

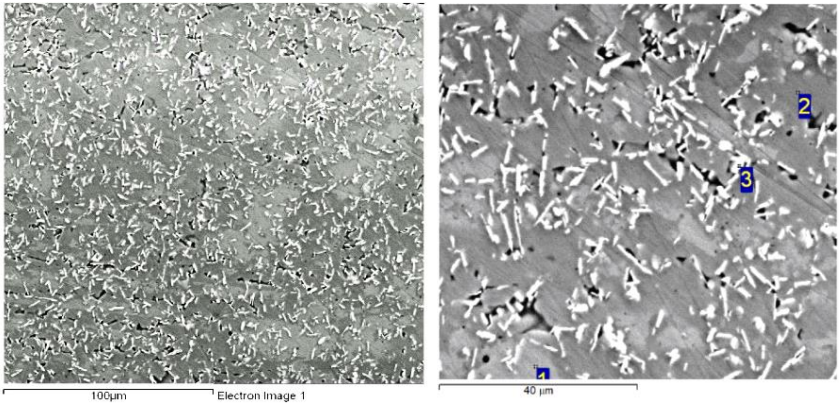


Fig. 3.6. The microstructure of obtained two-phase (γ/α_2) *TiAl* alloy

The results of X-ray diffraction analysis showed that in the synthesized state, the γ-*TiAl* alloy consists of two phases: *TiAl* (γ-phase) and Ti_3Al (α_2-phase). In a given alloy, the volume fraction of the α_2-phase relative to the γ-phase is about 20 %. The diffraction pattern of the synthesized γ-*TiAl* alloy is shown in **Fig. 3.7.** The X-ray diffraction analysis method found that on the diffractograms of the samples after the synthesis there are peaks of γ-*TiAl* (interplanar distances $d = 2.2063$, 1.9120, 1.2811, 1.1777, 1.1468 Å) and weak reflections of Ti_3Al peaks ($d = 2.1036$, 1.3902 Å). That is, the phase composition of the investigated synthesized γ-*TiAl* alloys is similar to that found earlier in papers [56, 57].

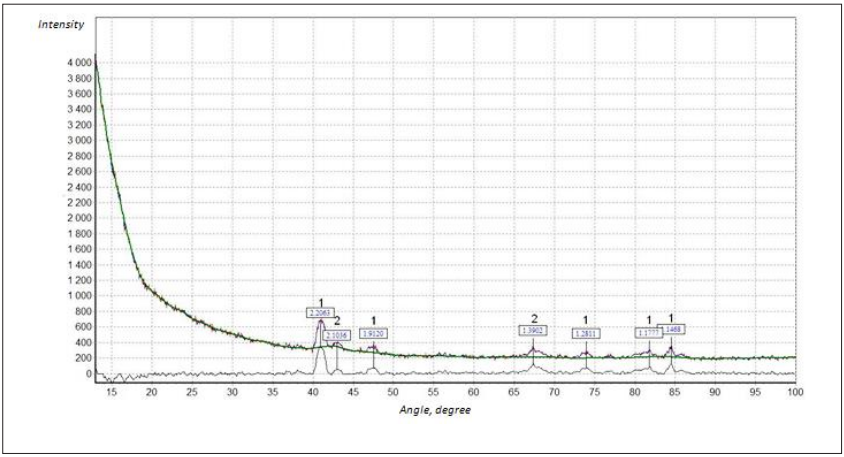


Fig. 3.7. The diffraction pattern of the synthesized γ-*TiAl* alloy:
1 – the phase of γ-*TiAl*; 2 – α_2-Ti_3Al

Metallographic studies have shown that the synthesis of the alloy formed a two-phase structure. In the alloy, there are single micropores, the presence of large pores and cracks are not detected. The microhardness of the alloy is HV 3000–4000 MPa. The results of microanalysis revealed a uniform and fine distribution of titanium aluminide *TiAl*. According to the microstructures, the *TiAl* system was predicted to be two-phase: *TiAl* (γ-phase) gray and Ti_3Al (α_2-phase) white. In addition, in the structure of the alloy, on the background of a two-phase structure, disperse light inclusions of various forms are formed, which are evenly distributed in the volume of the matrix and have an increased content of titanium.

The chemical composition of the γ-*TiAl* alloy in different areas of the surface microshields was determined using the microrentgenospectral analysis (**Fig. 3.8**). The content of components was determined in atomic and mass percentages. As a result of the quantitative analysis it was found that the matrix (gray area) of the

γ-*TiAl* alloy has a composition in mass percentage: 42.13 % *Al* and 57.52 % *Ti*, which corresponds to the intermetallic phase of *TiAl* (γ-phase) (Fig. 3.8, *a*, spectrum 3). Extruded, white in the region, according to the results of microrentense spectral analysis (Fig. 3.8, *a*, spectrum 7) are intermetallics of α_2-Ti_3Al composition, with elements content in mass percentages: 22.62 % *Al* and 77.38 % *Ti*.

Near these inclusions, and in some cases and within them, the dispersed phases are found. Indications of local chemical analysis (Fig. 3.8, *a*, Spectrum 1) allowed them to be identified as α_2-Ti_3Al

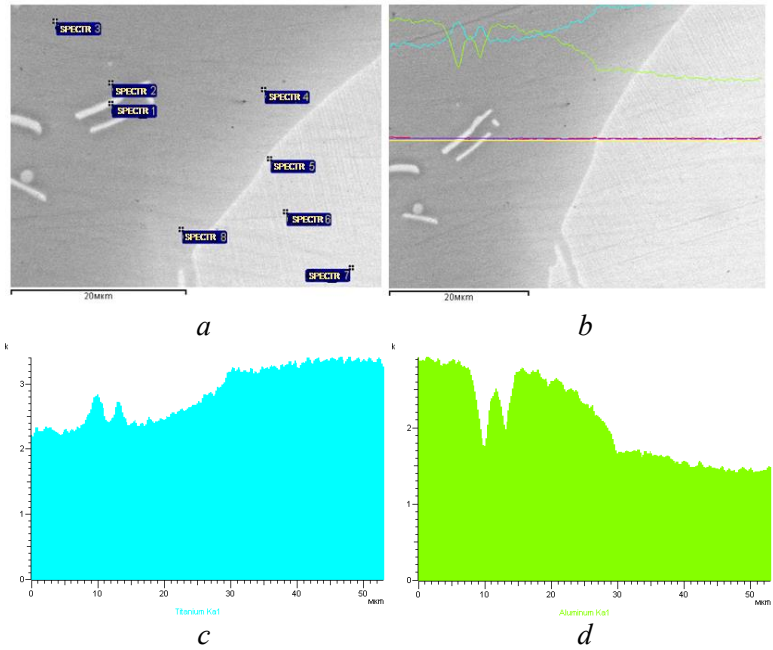


Fig. 3.8. Results of microrentense-spatial analysis of γ-*TiAl* alloy:
a – location of determination of local chemical analysis of alloy;
b – change in the intensity of radiation in motion along the line;
c – distribution of titanium; *d* – distribution of aluminum

intermetallic substances containing 28.77 % *Al* and 71.23 % *Ti*. This is consistent with the results obtained in [60].

To clarify the data, micro-X-ray spectral analysis was performed along the line (Fig. 3.8, *b*). In the left part of the scanning trajectory are marked peaks of aluminum, which confirms the crystallization of the intermetallic phase in the alloy in the form of monoaluminidum titanium γ-*TiAl*. Further motion in the trajectory of scanning (Fig. 3.8, *c*) in the region of the extended form shows the increase in the content of titanium and the reduction of the content of aluminum (Fig. 3.8, *d*). This is consistent with the results of the local analysis and indicates the formation of the intermetal phase α_2-Ti_3Al.

The results of the microrentense-spectral analysis allowed to prove the production of a two-phase structure in the γ-*TiAl* alloy with the intermetallic phases γ-*TiAl* and α_2-Ti_3Al. It was also found that due to the high temperature of synthesis, the process of self-cleaning of the product from impurities takes place in the IMS, which minimizes the probability of the appearance of impurity atoms. The determination of the SUPRA 40WDS microscope in the SHS alloy of oxygen, nitrogen and other impurities showed that they are missing or not exceeding one thousandth of a percent.

Doping with a refractory *Nb* is the most important for the application of products where high temperature strength and oxidation resistance, as well as room temperature ductility, are critical. The niobium addition has a significant effect on the volume of α_2-phase fraction and average interlam distance. Thus, doping of γ-*TiAl* alloys with niobium (7–8 % by weight) and an increasing of plastic deformation degree in conditions of extrusion at a load of 100 MPa allows to significantly reduce the grain size in the final product (to 0.2–0.3 μm). It leads to submicrocrystalline granular structure formation in the intermetallic alloy.

The microstructure analyze of synthesized *Ti-Al-Nb* alloy has shown that the formation features of thinner structures is in increased

content of the β-stabilizing element. As a result, a thin composite texture is formed consisting of parallel alternating lamellae of two different crystalline phases: tetragonal γ-phase (*TiAl*) and hexagonal α_2-phase (Ti_3Al) (**Fig. 3.9**). Thus, a two-level structure is formed: each polycrystalline α-grain forms a bounded lamellar colony consisting of thin lamellas with an intermolecular distance of 500 nm.

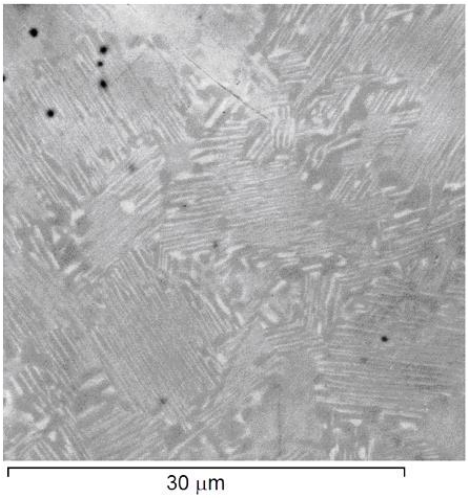


Fig. 3.9. The microstructure of obtained *Ti-Al-Nb* alloy

The further calculation is aimed at studying the strength evaluation of alloys according to the Hall-Patch model. The given theory gives the following dependence of short-term limit stress (σ) on the grain size (*d*) and lamellae thickness (λ) during faze segregation (**Fig. 3.10**).

$$\sigma = \sigma_0 + \frac{k_d}{\sqrt{d}} + \frac{k_\lambda}{\sqrt{\lambda}},$$

where: σ_0 is the yield stress of non-textured material, k_d and k_λ are Hall-Patch constants of grain and lamellae accordingly.

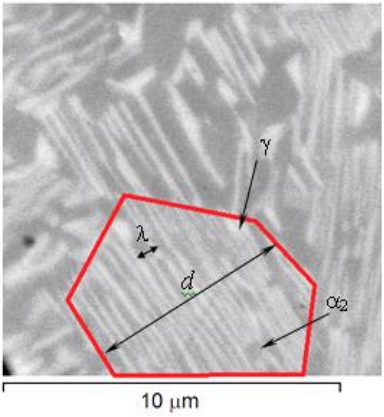


Fig. 3.10. The grain size d and lamellar colonies distance λ in the *Ti-Al-Nb* system

The mechanical properties of the two-level structure can be improved upon the transition of parameters of structural-phase segregation d and λ from micron to nano-dimensional level. In addition to the thermal conditions, the segregation parameters are optimized by doping affects on values of the coefficients k_d, k_λ. The best result is achieved with the joint action of these factors.

The limit strength of fully lamellar intermetallic alloys with colony sizes ranging from $d = 10$ to 50 μm and lamellar spacings from $\lambda = 100$ to 500 nm was studied. As noted in work [58], an apparent Hall-Petch constant of $k_d = 2.1$ MPa · m$^{1/2}$ was previously determined when the limit stresses were ranked against the colony size. It has been recognized that the lamellar spacing is proportional to grain size d and limit stress is governed by λ. In order to make this idea quantitative, the authors proposed an analytical model for the limit stress of lamellar material that involves two Hall-Petch constants, which account for the effects of the grain boundaries ($k_d = 0.91$ MPa · m$^{1/2}$) and the lamellae interfaces ($k_\lambda = 0.45$ MPa · m$^{1/2}$).

The results intermetallic alloys strength calculations are presented on **Fig. 3.11**. Calculations, which were carried out using the Hall-Petch model [59], show the possibility of obtaining structural components with a size of 10–12 μm with a tensile strength of more than 1800 MPa for *Ti-Al-Nb* and 800 MPa for Ti-Al. Analysis of literature data showed that the strength limits values of these materials are close or even exceeding the obtained values for a certain size of structural components, which indicates the reliability of the results. It is important to note that the plastic anisotropy of the lamellar morphology can also become evident in the strength properties, which will be the subject of our further research.

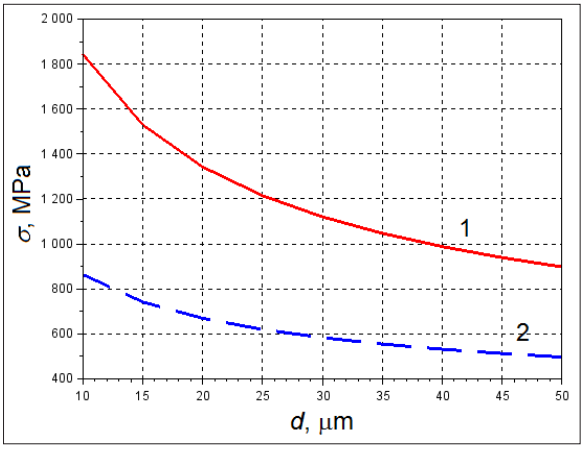


Fig. 3.11. The dependence of stress limit σ on grain size *d* for *Ti-Al-Nb* (1) and *Ti-Al* (2)

It is found that high-temperature synthesis of intermetallic alloy *TiAl* powder in a mixture of pure elements in terms of TCP-process with thermal explosion provides a synthesis of intermetallic product with an average grain size ~30 microns. The increasing of plastic deformation degree will significantly reduce the grain size in the final

product and even will form intermetallic alloy with sub-microcrystal granular structure.

Microstructure analize has shown that doping of γ-*TiAl* alloys with niobium (7–8 % by weight) and an increasing of plastic deformation degree in conditions of extrusion at a load of 100 MPa allows to significantly reduce the grain size in the final product (to 10–12 μm) and form two-level structure with nanolamellar colony with distance up to 500 nm.

Calculations, carried out using the Hall-Petch model, show that obtained *Ti-Al-Nb* alloy with lamellae nanostructure has limit strength up to 1800 MPa which in 3 times more than in *Ti-Al* alloy. Analysis of literature data show that the strength limits values of these materials are close or even exceeding the obtained values for a certain size of structural components, which indicates the reliability of the results.

3.4. Development of intermetallic alloys with high level of physico-mechanical and operational properties

He main attention of developers of intermetallic γ-*TiAl* alloys in the last two decades has been concentrated on achieving the optimal combination of mechanical properties by varying the microstructure from completely lamellar to duplex with different grain sizes and plate thicknesses [60]. Depending on the aluminum content, γ-*TiAl*-based alloys are divided into two groups: single-phase γ-alloys (50–52 % Al) and biphase $\gamma + \alpha_2$ alloys (44–49 % *Al*). Three main types of intermetallic structure based on titanium aluminides: lamellar (lamellar), recrystallized (globular) and bimodal (duplex)) are distinguished depending on the technology for obtaining blanks, hot deformation modes and thermal processing of two-phase alloys. In the foreign literature there is a classification into four types of structure: near-gamma, duplex, nearly-lamellar, fullylamellar. To date, there

is no universal γ-*TiAl* alloy, the characteristics of which would fully satisfy the requirements of the aerospace and aerospace engineering developers for the whole spectrum of operational properties. Optimization of the chemical composition and microstructure of these materials led to the generation of their three generations (composition in atomic percent) [61–63].

1st generation – *Ti-48Al-1V-0.3C*.

2nd generation – *Ti*-(45–48) *Al*-(1–3)*X*-(2–5)*Y*-(<1)*Z*.

where: *X* = *Cr, Mn, V; Y* = *Nb, Ta, W, Mo; Z* = *Si, B, C*.

3rd generation – *Ti-(45–47) Al-(5–10) Nb-(<1) B, C*.

Industrial γ-*TiAl* alloys of the second generation contain at least one *X*-element and one *Y*-element, which increase the resistance to oxidation and creep. Like high-temperature nickel superalloys, they can contain up to eight alloying elements. These alloys have good workability, satisfactory strength properties, elongation at a stretching of 1–3 % at room temperature, fracture toughness from 10 to 25 MPa/m [60]. However, according to the creep characteristics, their use is limited to 700 °C, especially during long-term operation. At temperatures above 700 °C, insufficient oxidation resistance can also be affected.

Alloys of the third generation are developed in order to increase their operating temperatures. The works are conducted in two directions: a) on the basis of alloys with a high content of niobium; b) development of dispersion-hardened alloys [61, 62]. *TiAl*-based alloys with niobium content from 5 to 10 % and small additives B and *C* are *TNB* [63]. These alloys have higher strength and oxidation resistance compared to second-generation alloys. In the opinion of the author [64], *TiAl*-based alloys can have an acceptable creep resistance up to a temperature of 750 °C with a duplex (lamellar-granular) structure, and up to 950 °C with a lamellar structure.

The latest trend in the development of technology for high-temperature γ-intermetallic compounds based on *TiAl* is associated with their special microstructuring, i.e. the decrease in both the mean

size of the primary polycrystalline grain and the thickness of the γ- and α_2-phase lamellae after post-crystallization solid-phase transformations occurring in accordance with the alloy state diagram of a specific chemical composition [60, 62, 65, 66]. Innovative γ-*TiAl* alloys (*TNM*-alloys) contain 42–46 at.% Aluminum, and as ligatures in the sum up to 10 at.% Transition metals. In addition to the obligatory *Nb*, such β-stabilizers as *Mo*, *Ta, Zr, Cr, W, V* can be used.

At the same time, to date, there are no strict analytical relationships connecting the parameters of the structure of *TiAl*-intermetallides and their composition with the mechanical strength characteristics of the material. The development of materials science in this area is at the level of empirical research, taking into account the qualitative laws, therefore when planning the work it is possible to be guided only by independent structural, composite and strength studies of samples in order to obtain empirical data. The most promising microstructure of the cast alloy is characterized by the presence of ultra-fine equiaxed grain-colonies completely filled with laminated *TiAl* and Ti_3Al-phase lamellae. This microstructure is characteristic of alloys based on *Ti-Al-Nb*.

The mechanical properties were determined on standard discontinuous specimens in accordance with GOST 1497-84 on a tearing machine MUP-20 at a load of 5 tons and the speed of movement of the active gripper 2.5 mm/min. During the test of the sample, a tensile diagram was recorded, fixing the relationship between the force acting on the sample P and the deformation induced by it Δl.

Optimization parameters:

Y_1 – ultimate strength (σ_s), MPa → max;

Y_2 – relative elongation (δ),%. > 4.

As independent variables, the content in the niobium alloy (X_1), the content of molybdenum (X_2), the content of the chromium mixture (X_3) were chosen. As the initial components, pure powders of titanium, aluminum, niobium, molybdenum and chromium were used.

Dispersion of powders was 50–100 microns. The batch preparation scheme included dosage, mixing, mold filling, pressing and heat treatment.

To obtain the quadratic coefficients of the regression equation, an orthogonal plan of the second order with the kernel 2^3 is used [68]. The calculated levels of variation intervals, the nature of their variation and the coding scheme are presented in **Table 3.1**. Niobium, applied at high concentrations, increases the amount of the α_2 phase in alloys, grinds the microstructure, increases the oxidation resistance. Chromium reduces the energy of the defects of the package, which leads to an increase in ductility at room temperature as a result of increasing the tendency of alloys to twinning. Molybdenum, which has a high β-stabilizing activity, grinds the grain.

Table 3.1 Factors studied

Characteristic	Factors		
	***Nb*, % wt.**	***Mo*, % wt.**	***Cr*, % wt.**
Code	X_1	X_2	X_3
Basic level	8	3	2
Variation interval	4	2	1
Lower level	4	1	1
Top level	12	5	3

As a result of regression analysis, according to the procedure considered in [68], equations were obtained showing the dependence of the mechanical properties of the γ-*TiAl* alloy on the content of alloying elements:

$$Y_1 = 1198{,}22 + 20X_1 + 12X_2 + 7X_3 - 147{,}78\,X_1^2 - 37{,}78\,X_2^2 - 12.78\,X_3^3 - \\ - 5X_1X_2 - 2{,}5X_1X_3 - 2{,}5X_2X_3; \qquad (3.13)$$

$$Y_2 = 3{,}89 + 1{,}02X_1 + 0{,}54X_2 - 0{,}08X_3 - 0{,}97\,X_1^2 - 0{,}37\,X_2^2 + 0{,}33\,X_3^3 - \\ - 0{,}16X_1X_2 + 0{,}04X_1X_3 - 0{,}01X_2X_3. \qquad (3.14)$$

Checking the significance of the regression coefficients by the Student's test and evaluating the adequacy of the model using the Fisher criterion are presented in **Table 3.2**.

The coefficients, the absolute value of which is equal to the confidence interval Δb or more, should be considered statistically significant. Statistically insignificant coefficients (in this case, b_{12}, b_{13}, b_{23}) can be excluded from models.

Table 3.2. Checking the results of regression analysis for relevance and relevance

Parameter	Response functions	
	Y_1	Y_2
Δb	10.14	0.10
t-test	2.78	2.78
F-test	6.09 > 3.69	6.09 > 6.02

Checking the adequacy of the models shows that they can be used to predict the values of the response functions for any values of the factors between the upper and lower levels. For this, it is advisable to go over to natural variables using the translation formula, which is presented in the following form [69]:

$$X_{ij}^{k} = \frac{X_{ij}^{n} - X_{ij}^{o}}{\Delta_i}, \tag{3.15}$$

where X_{ij}^{k} – coded value of the studied *i*-th factor in the *j*-th equation; X_{ij}^{n} – natural value of the studied *i*-th factor in the *j*-th equation; X_{ij}^{o} – value of the studied i-th factor in the j-th equation at the ground level; Δi – value of the variation interval of the i-factor studied.

By replacing the variables X_i in equations (3.13) – (3.14) with the right-hand side of equation (3.15) and the subsequent reduction of similar ones, we obtain natural equations describing the effect of the content of alloying elements on the mechanical properties of γ-*TiAl* alloys:

$$\sigma_s = 413 + 152{,}78Nb + 62.67Mo + 51{,}11Cr - 9.23Nb^2 - 9{,}44Mo^2 - 12{,}78Cr^2, \quad (3.16)$$

$$\delta = -2{,}8 + 1{,}28Nb + 0{,}98Mo - 1{,}33Cr - 0{,}06Nb^2 - 0{,}1Mo^2 + 0{,}33Cr^2 - 0{,}02NbMo. \quad (3.17)$$

As can be seen from equation (3.16), the dependence of the ultimate strength on the alloying elements is elliptical, without their mutual influence. Taking into account the above, the method of gradient descent in the applied program for the solution of engineering-mathematical problems SciLab [68] obtained the optimum point max (σ_s): $\sigma_s(8{,}27;3{,}18;2) = 1199{,}86$ MPa.

Below are graphs of the dependence of the strength limit on the concentration of alloying elements (**Fig. 3.12–3.14**). For each of the graphs, the value of the third factor was taken at the optimal level.

From the analysis of the equations obtained it is clear that the most strongly mechanical properties of γ-*TiAl* alloys depend on the content of niobium and molybdenum in the alloy. Noticeably affects the ratio between the amount of niobium and molybdenum. The representation of the results of the experiment by a polynomial of the second degree proved to be justified – a significant part of the nonlinear terms here is significantly different from zero. Since nonlinear regression coefficients have the same signs, the response surface is an ellipsoid, and its center is an extremum, with a maximum, since the regression coefficients are negative. As expected in the formulation of the problem, the optimal content of alloying elements of the analyzed composition lies in the experimental region, and near its center.

Equation (3.17) is an elliptic paraboloid. The extremum with respect to the third factor, taking into account the range of admissible values, is in the maximum permissible concentration ($Cr = 3$). Having carried out numerical optimization with respect to the two remaining factors, we obtain the following optimum point max (δ): $(9{,}89;4{,}26;3) = 4{,}63$ %.

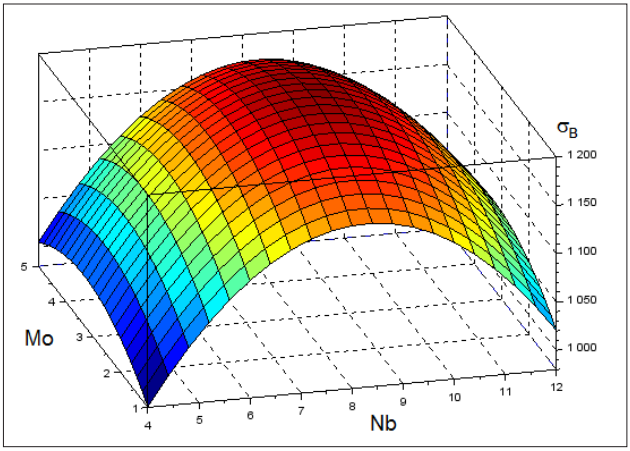


Fig. 3.12. Function (3.16) graph with value of $Cr = 2$

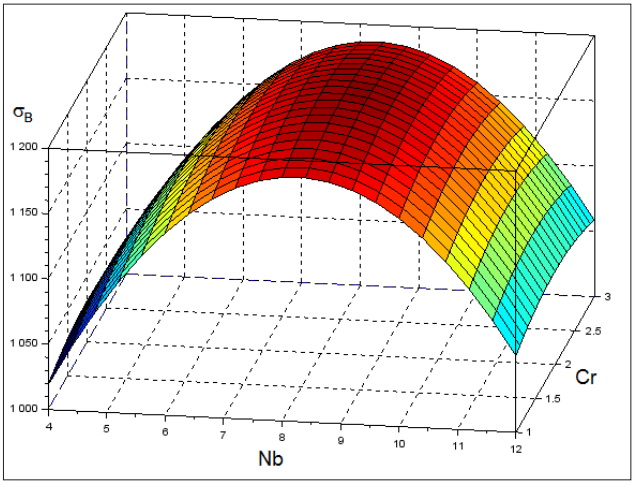


Fig. 3.13. Function (3.16) graph with value of $Mo = 3{,}18$

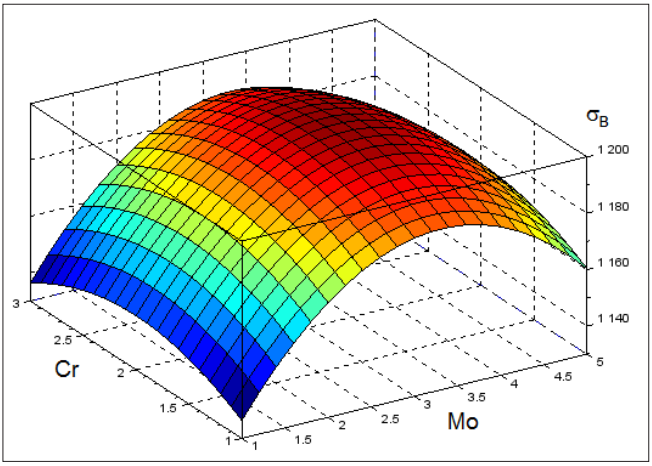
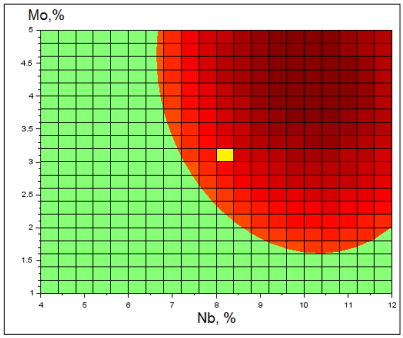


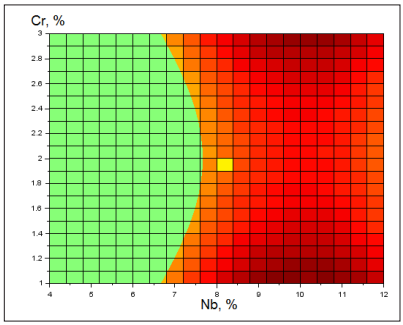
Fig. 3.14. Function (3.16) graph with value of *Nb* = 8,27

Fig. 3.15 shows the admissible values of equation (3.17), taking into account the optimization parameter (> 4 %). As can be seen from Fig. 3.15, the optimal value of the tensile strength lies in the rational region of the plasticity function.

Thus, the recommended optimum composition of the intermetallic γ-*TiAl* alloy, wt. %: aluminum – 30 %, niobium – 8.3 %, molybdenum – 3.18 %, chromium – 2 %, titanium – the rest (Formula *Ti-44Al-4Nb-2Mo-1Cr*).



a



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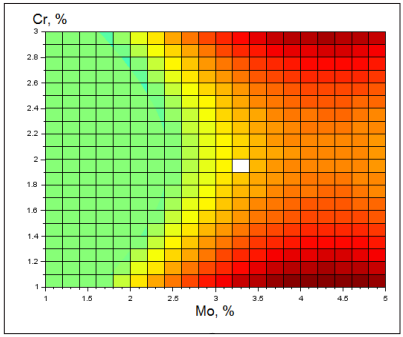

c

Fig. 3.15. Function (3.17) phase plate with value of $Cr = 3$(a), $Mo = 4{,}26$ (b), $Nb = 9{,}89$(c)