

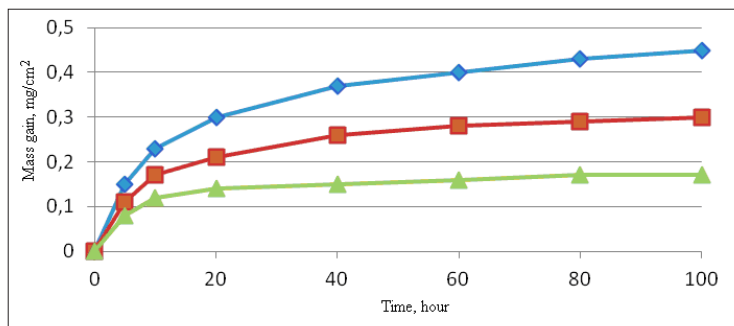
4. PRACTICAL VALUE OF MATERIALS OBTAINED BY THE THERMOCHEMICAL PRESSING METHOD

4.1. Research on heat resistance of intermetallic γ -TiAl alloy

In order to determine the operational characteristics of the obtained intermetallics, heat resistance studies of the developed samples of the γ -TiAl alloy were conducted in comparison with the existing titanium alloys VT-1-00 and VT-20. To carry out heat resistance research, samples of various titanium alloys (VT-1-00 and VT20) and intermetallics (γ -TiAl) with dimensions of 10x10x1 mm were cut. Before oxidation, these samples were mechanically cleaned with sandpaper, washed with distilled water, and subjected to ultrasonic cleaning in ethyl alcohol for 10 minutes. Then the processed samples were subjected to isothermal and thermocyclic oxidation at a temperature of 700 °C in a laboratory furnace SNOL 1,6,2,0.0,8/9. During isothermal oxidation, the samples were placed on levers for the purpose of constant weight measurement [63].

During the isothermal heat resistance test at a temperature of 700°C of samples of titanium alloys VT-1-00, VT-20 and γ -TiAl, a parabolic dependence was obtained, presented in **Fig. 4.1**. From the dependence curves of heat resistance, it can be seen that the largest increase in mass is observed in the VT-1-00 alloy. When approximating the obtained results, it was established that further aging at 700 °C significantly affects the oxidation of the material [64]. Alloy VT-20 also increases in mass, however, unlike VT-1-00, further diffusion of oxygen stops, and the increase in mass exceeds 0.35 mg/cm². γ -TiAl aluminide at this temperature has the lowest mass gain and does not exceed 0.2 mg/cm². In order to fully describe

the oxidation process of the samples, it is necessary to analyze more carefully the heat resistance measurements of each of the given samples.



1 – VT-1-00, 2 – VT-20, 3 – γ -TiAl

Fig. 4.1. Heat resistance of alloys at 700 °C

After measuring the VT-1-00 alloy sample, a porous layer of TiO_2 is formed on its surface (**Fig. 4.2**). Because of this, oxygen can quickly diffuse through the porous oxide layer deep into the titanium material. This explains the presence of oxygen under the porous layer (**Fig. 4.3**). As a result of measuring the VT-1-00 sample for heat resistance, a porous oxide layer with a thickness of 30 microns was formed under the influence of oxygen. This causes cracking of the transition oxygen sublayer [65].

As can be seen from (**Fig. 4.4**), the microhardness of the oxide surface layer is 4 times higher than the microhardness of the titanium substrate. This surface oxide film can lead to premature failure of the part during cyclic loads.

It is known from the literature that in the process of oxidation of titanium alloys, the formation of titanium oxides TiO , Ti_2O_3 , Ti_3O_5 and TiO_2 is possible. The thermodynamic probabilities of the formation of

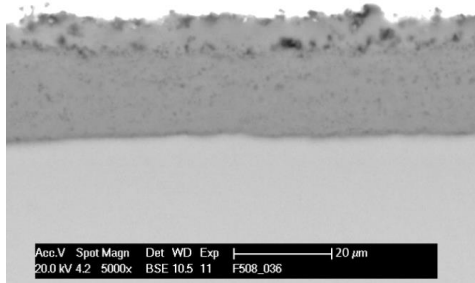


Fig. 4.2. Microstructure of titanium alloy VT-1-00 with a surface oxide film

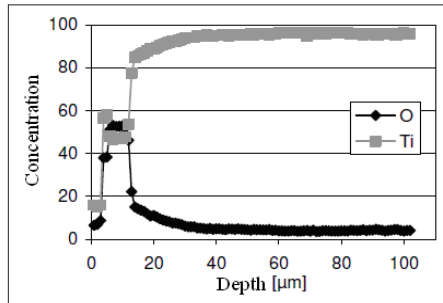


Fig. 4.3. Distribution of elements by layer thickness in the VT-1-00 alloy

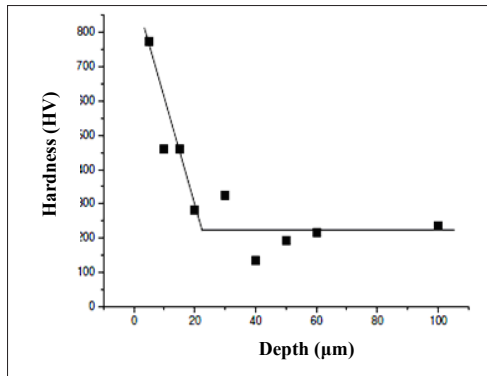
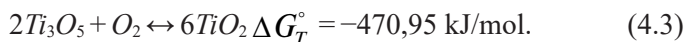
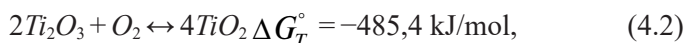
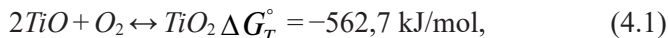


Fig. 4.4. Vickers microhardness distribution in the VT-1-00 alloy

one or another titanium oxide are close (the difference in the changes in the free reaction (4.5)–(4.7) is insignificant), however, at high oxidation temperatures, the oxidation of lower oxides to the higher oxide TiO_2 is possible according to the reactions:

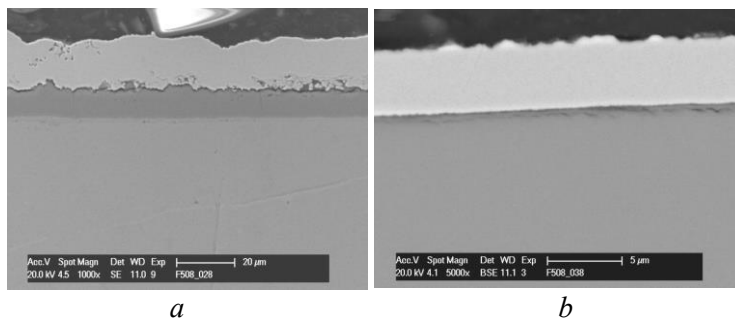


The probability of such processes is indicated by the negative values of the change in Gibbs free energy calculated for a temperature of 1273 K.

Alloying it with aluminum contributes to the reduction of mass gain and, accordingly, to the reduction of diffusion penetration of oxygen deep into the titanium alloy [66].

Additional doping with aluminum leads to the formation of a protective Al_2O_3 film, which interferes with the diffusion activity of oxygen. This can be seen in **Fig. 4.7**, where the VT-20 alloy has a smaller oxide layer and a characteristic Al_2O_3 film. However, an insufficient amount of aluminum for the complete formation of a protective film leads to the penetration of oxygen and the formation of an oxide layer.

The hardness of the surface layer was, as in the previous case, 750 HB, and the hardness of the inner layers of the VT-20 alloy was 1.8 GPa, which coincides with the literature data. The oxide layer in the obtained titanium aluminide $TiAl$ is almost invisible. A thin oxide film is difficult to see in the SEM photograph (**Fig. 4.5**). However, X-ray spectral studies showed a slight intensity of oxygen on the surface of the studied sample, but without its diffusion deep into the material. The hardness of the material is unchanged by the depth of analysis and is about 1.5 GPa.



a – BT-20, *b* – TiAl

Fig. 4.5. Microstructure of the surface layer of the alloy

Thus, at a research temperature of 700 °C, the heat resistance of titanium aluminide is twice as high as that of the VT-20 alloy and three times that of VT-1-00 due to the aluminum content and the formation of a protective oxide film that prevents oxygen from penetrating deep into the material.

4.2. Research of intermetallic alloys for aerospace engineering parts

Intermetallics of *Ti-Al* systems are heat-resistant and corrosion-resistant compounds, which are promising for use in heat-resistant alloys, and are also of interest from the point of view of studying the processes of modification and doping of aluminum with titanium. Titanium aluminides are a group of new instrumental and structural materials, which are obtained by thermochemical pressing technology, described in previous sections. The characteristics of corrosion resistance and heat resistance that these materials possess allow them to be used in many areas of industry (aircraft, rocket engineering, mechanical engineering, etc.) [66–75].

In the field of structural, including cast, titanium alloys, the task of increasing the resource and reliability is solved by the creation of a new generation of complex-alloyed alloys (type VT-20) with increased characteristics of the endurance limit by 30% and crack resistance by 20%, while reducing the cost of the alloy by 20...30% due to full transition to domestic raw materials and non-deficient alloying components (absence of molybdenum and vanadium) [75].

At this time, the design, technological and materials science work on the problem of creating a new, sixth generation engine is underway. At the same time, the task of increasing the performance of materials under the conditions of solid complex effects of high temperatures, stresses and an aggressive environment is one of the most important. In the engine of the sixth generation, it is necessary to ensure a thrust/mass ratio = 20:1. For comparison, this ratio for engines of the fourth generation (1970–1975) equals 8:1, and for modern engines of the fifth generation (1985–2000) – 10:1 [76].

The use of new classes of materials and technologies should ensure:

- an increase in the operating gas temperature of new generation engines from 1573...1673 K to 1873...2073 K;
- reduction of fuel consumption from 0.6 to 0.4 kg of fuel/kg of thrust per hour;
- increase in thrust from 28,000 to 40,000 kgf;
- increasing the reliability and resource of disks by 2...3 times, temperature by 323–343 K, reducing the weight of disks by 10...15%;
- reducing consumption of scarce alloying elements (*W, Nb, Re*, etc.).

To increase the resource and reliability of heat-resistant titanium alloys, first of all, it is necessary to fully realize the potential of domestic alloys due to the improvement of technological schemes for the production of serial products (alloys VT8M1, VT8-1, VT25V, VT 18).

At the same time, potential opportunities for further increasing the heat resistance of titanium alloys at temperatures > 893 K remain extremely small, and alloying opportunities are practically exhausted.

The main prospects in the development and development of a new generation of structural heat-resistant titanium alloys with increased density, before oxidation, are related to the development of intermetallic compounds based on the *TiAl* system for operation at temperatures of 873...1073 K.

In the world technical literature, the term “superalloys” was first introduced in 1972. will be used to denote heat-resistant and corrosion-resistant alloys based on *Ni*, *Al*, *Ti*.

Superalloys work in gas turbines of air, marine, automobile transport, tank engines, industrial gas turbines in rocket engines, space vehicles, nuclear reactors, and petrochemical equipment.

Basically, superalloys are used as heat-resistant materials, but about 15...20% of these alloys are used as corrosion-resistant materials in the chemical, petrochemical, thermal and nuclear power industries, in the production of glass, paper pulp, and means of combating environmental pollution.

Along with superalloys, titanium aluminides are quite promising structural materials for work in extreme conditions, the advantages of which are:

- a high absolute level of service properties and characteristics, comparable to the level of properties of traditional competing materials;
- low density (specific gravity) and a high level of specific properties related to a unit of density (specific weight), which exceeds the value of these properties in competing materials (nickel and titanium alloys, steels);
- relative cheapness compared to competing materials.

Heat-resistant superalloys in the 90s of the XX century. accounted for 40...50% of the mass of gas turbine structures: gas turbine units (GTU) and gas turbine engines (GTE). According to forecasts, this share will drop to 30% by 2020, because about 15% will come to new classes of materials – titanium aluminides [70].

The unique combination of properties of titanium aluminides makes them particularly attractive, and they are considered as next-generation materials. Rational use of secondary energy (coke, blast furnace, converter and ferroalloy gases, natural gas energy, heat of hot agglomerate, etc.) and material (metal scrap, landfill slag, gas cleaning dust, pickling solutions, carbon dioxide, etc.) resources is one of the ways to reduce energy and material intensity of the metallurgical industry. [71, 75, 77, 78]. According to works [79–81], alloys of the $TiAl$ system have a density of 4.2 and 3.8 % g/cm^3 , respectively. Up to temperatures of 973...1073 K, they maintain high values of σ_0 . Young's modulus E and good heat resistance (due to the high aluminum content). Due to the low density, their specific properties (σ_0 , E) at these temperatures significantly exceed the properties of traditional nickel and titanium alloys. Titanium aluminides are approximately 3 times cheaper than nickel alloys that work for a long time at temperatures up to 973 K, and based on a unit of specific strength, they are 5 times cheaper than the corresponding nickel alloys (XH55BMKIO).

Compact titanium aluminides are obtained either in the cast state, using the technology of vacuum-induction remelting, or by hot isostatic pressing of powders. A more promising method of obtaining intermetallic compounds of the $TiAl$ system is thermochemical pressing [82].

The method is carried out as follows. The initial intermetallic mixture of powders is prepared, the blank is pressed with a relative density of 0.6–0.8. The relative density significantly affects the grain size and conditions of high-temperature synthesis and has an extreme character. A decrease in density leads to a frontal mode of combustion and a decrease in the intensity of the exothermic reaction. A higher density leads to blockage of gases released from the adsorbed and dissolved state. Such clogging prevents effective compaction of the material, increases its residual porosity and changes its chemical composition. The resulting workpiece is placed in a reaction mold

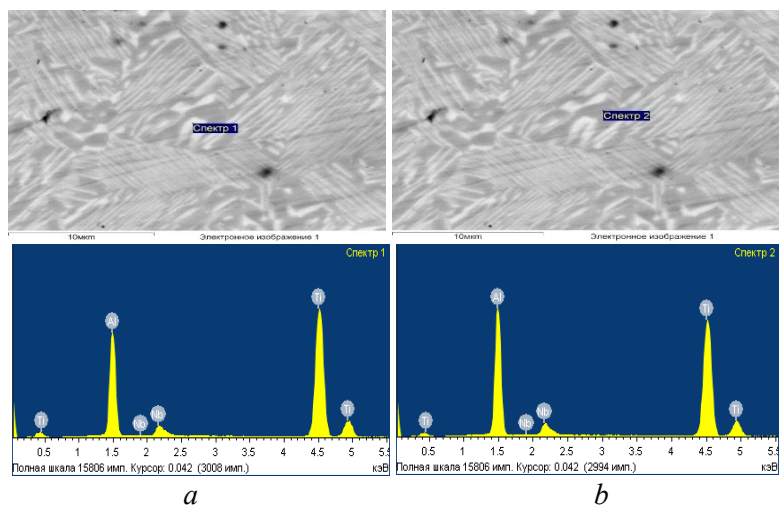
in an inert powder medium of a loose heat insulator, filled with an inert gas medium, where it is heated evenly. The presence of a heat insulator is mandatory for small-sized blanks that have a short cooling time of synthesis products after the end of combustion. Without thermal insulation, such blanks are cooled due to heat dissipation into the steel mold faster than the process of compaction of synthesis products occurs due to compaction. Further, with uniform heating, the workpiece self-heats. Due to the exponential dependence of the reaction rate on the temperature, the temperature rise in the volume of the workpiece proceeds with a progressive self-acceleration and ends with a sharp temperature jump, the self-ignition process is initiated, as a result of which synthesis begins in the mixture. During thermal self-ignition due to self-heating, high temperatures of the sample are reached almost simultaneously in the full volume of the workpiece, at which the synthesis of the product is quickly completed. After the passage of the combustion wave, plastic deformation of the synthesis product is carried out in the high-temperature region at a degree of deformation of 20...30% and a holding time under pressure of 3...5 s. The amount of deformation is an effective tool for controlling the parameters of the lamellar structure of intermetallic alloys. However, when the critical value of the degree of deformation is exceeded, the material transitions into the region of brittle failure and the workpiece cracks. At the end of the deformation, isothermal aging is carried out at a temperature of 0.6...0.7 from the melting temperature of the intermetallic for 1.5...2 hours to adjust the ratio of the structural components of the intermetallic alloy.

The method of obtaining intermetallic γ -TiAl alloy was tested in industrial conditions. Pure powders of titanium (57...63 wt. %), aluminum (30...35 wt. %) and niobium (7...8 wt. %) were used as starting components. The dispersion of the powders was 50...100 μm . The batch preparation scheme included dosing, mixing, filling the mold and pressing a rectangular blank with a diameter of 20 mm and

a height of 20 mm with a relative density of 0.65. The reaction mold is adapted for two-sided pressing. The lower punch was installed. Electrocorundum powder was poured to a height of 30–40 mm. The workpiece was installed in a vertical layout. I fell asleep on top with electrocorundum powder. The upper punch was installed and primary compaction was carried out on a press at a specific pressure of 10 MPa. The prepared mold was installed in a vertical furnace with a working diameter 5...15 mm larger than the diameter of the mold. The furnace together with the mold was installed on a P-250 hydraulic press. The furnace was turned on and the temperature rose at a rate of 30...50 °C/min. The temperature was raised before the start of the high-temperature synthesis process. During the synthesis of the charge, the released gases were discharged when their pressure reached 0.15 MPa. After thermal self-ignition took place, plastic deformation of the workpiece was carried out with 27.8% crimping to the specified density and exposure at a temperature of 1100 °C for 1.5 hours at a pressure of 16 MPa. At the end of the exposure, the reactor was evacuated for 15 minutes to 0.2 mm Hg. and cooled for 2 hours [83].

Analysis of the microstructure of the obtained synthesized titanium aluminides showed that a feature of the formation of finer structures during the high-temperature synthesis of compositions based on *Ti-Al-Nb* is a lamellar microstructure with a small size of colonies and a nanocrystalline interlamellar distance (**Fig. 4.6, a**).

As a result, a thin composite texture is formed, consisting of alternating parallel lamellae of two different crystal phases: tetragonal γ -phase (*TiAl*) and hexagonal α_2 -phase (*Ti₃Al*). Thus, a two-level structure is formed: each polycrystalline α -grain forms a limited lamellar colony, which consists of thin lamellae with an interlamella distance of $\lambda = 500...550$ nm (Fig. 4.6, b). An increase in the degree of deformation of the intermetallic product synthesized under pressure made it possible to reduce the grain size in the final product by an order of magnitude (to $d = 10...12$ μm).



a – spectrum 1; *b* – spectrum 2

Fig. 4.6. Microstructure with point selection of micro-X-ray spectral analysis for intermetallic γ -TiAl alloy

The use of the proposed method for obtaining intermetallic alloys in comparison with existing methods showed that under the conditions of interaction of synthesis processes and plastic deformation of the synthesis product, it is possible to obtain a compact intermetallic alloy with a highly dispersed structure, the grain size of which is significantly smaller than in alloys obtained by casting methods (size grains $d \sim 100 \dots 150 \mu\text{m}$), sintering ($d \sim 50 \dots 75 \mu\text{m}$) or shock wave action ($d \sim 20 \dots 35 \mu\text{m}$). The method provides the possibility of obtaining intermetallic alloys of a more complex nature and waste-free production.

In order to assess the possibility of using alloys based on titanium intermetallics in the design of gas turbine engines, an analysis of the strength and reliability indicators of the compressor blades of a modern

aircraft engine, made of an alloy based on titanium aluminide, was performed. The stress-strain state of the blade feather was determined as a result of calculation by the finite element method. For the material model, the mechanical properties of the “gamma” alloy, which has a two-phase structure, are given in **Table 4.1**.

Table 4.1. Mechanical and physical properties of the *Ti-Al-Nb* alloy

<i>E</i> , MPa	ρ , kg/m ³	σ_b , MPa	$\sigma_{0.2}$, MPa	μ	δ , %
$0,95 \cdot 10^5$	3800	1200	850	0.3	4

The change in the stress-strain state of the vanes made of alloys based on aluminides in comparison with the vanes made of titanium and iron-nickel alloys, which are produced in series, and, therefore, the indicators of strength and reliability, is associated with a simultaneous change in their main physical and mechanical characteristics. On the one hand, they are characterized by a lower value of density and modulus of elasticity (Table 4.1.), which leads to a decrease in the level of operating stresses. On the other hand, the maximum allowable stresses for such alloys are lower than, for example, for iron-nickel alloys [84]. Thus, in order to evaluate the effectiveness of the use of alloys based on intermetallics, it is necessary to evaluate the strength and reliability of the parts made from them. The calculated values of the field of stress distribution in the front of the blade during take-off operation of the engine are shown in **Fig. 4.7**.

When calculating the strength of the blade, we make the following assumptions:

- we consider the blade as a cantilever beam rigidly hammered into the rim of the disc;
- stresses are determined for each type of deformation separately;
- the temperature in the cross-section of the blade feather is assumed to be the same, i.e. there are no temperature stresses;
- the scapula is considered rigid, and the deformation of the scapula under the action of forces and moments is neglected;

– we assume that the deformations of the scapula occur in the elastic zone, that is, the stresses in the scapula do not exceed the limit of proportionality.

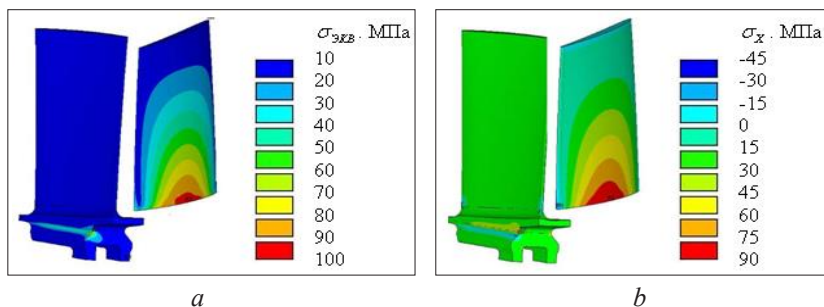


Fig. 4.7. Fields of distribution of equivalent (*a*) and radial (*b*) stresses in the tip of the compressor blade of the gas turbine engine made of titanium aluminide-based alloy in the take-off mode of operation of the gas turbine engine

The calculation of the strength reserves for the maximum stresses of the vane blade with the calculation of the action of variable and constant stresses showed that it is in the range that satisfies the requirements for the working blades of the compressor [84].

The developed technology for obtaining materials on an intermetallic basis was tested in the conditions of Motor Sich JSC. The results of the tests showed the advantages of using the proposed method in creating heat-resistant, dense materials on an intermetallic basis. Reliability assessment of high-pressure compressor blades of civil aviation gas turbine engines (D-436-148, D-18T, D-136) and small gas turbine engines for unmanned aerial vehicles (MS-400) showed the possibility of using intermetallic alloys based on titanium aluminides for compressor rotor blades of the last stages instead of heat-resistant alloys based on titanium and iron-nickel. Replacing parts made of nickel alloys operating in the temperature

range of 500...600 °C with parts made of alloys based on titanium aluminides will allow to reduce the mass of the GTE rotor structure by 1.5...2 times and reduce material costs by 20...35 %.

4.3. Study of the possibility of using intermetallic catalysts in the oxidation processes of carbon monoxide (II) and hydrocarbons

On the basis of the conducted research and developed technological processes for the formation of an intermetallic catalyst, a patent of Ukraine was obtained and its research and industrial testing was carried out in the conditions of PrT “Ukrgrafit” (Zaporizhzhia).

The method is carried out as follows. The initial intermetallic mixture is prepared from aluminum and nickel powders, the workpiece is pressed with a relative density of 0.5. The resulting blank is placed in a hot pressing matrix, filled with an inert medium, where it is heated evenly. With uniform heating, the workpiece self-heats. Due to the exponential dependence of the reaction rate on temperature, the temperature rise in the volume of the workpiece proceeds with progressive self-acceleration and ends with a sharp temperature jump, the self-ignition process is initiated, as a result of which self-propagating high-temperature synthesis begins in the mixture. During thermal self-ignition due to self-heating, high temperatures of the sample are reached almost simultaneously in the full volume of the workpiece, at which the synthesis of the product is quickly completed. After passing the combustion wave, the blanks are held at a temperature of 390...460 °C for 0.5...1 hour. At the heat treatment stage, the resulting product is pressed. The holding temperature of 390...460 °C is determined by the melting temperature of aluminum and is 0.6...0.7 of its melting temperature Ni_2Al_3 .

An increase in the holding temperature above 460 °C leads to the formation of the Ni_2Al_3 phase. The Ni_2Al_3 phase has a specific activity 1.8...3.4 times lower than that of $NiAl_3$. The low activity of the Ni_2Al_3 catalyst is due to the low degree of leaching of the mentioned aluminide.

An increase in the holding time of more than 1 hour reduces the porosity of the catalyst, the value of the average radius and the proportion of transitional pores, less than 0.5 hours does not ensure obtaining a more uniform phase composition of the catalyst.

After heat treatment, an intermetallic alloy of the required composition with a very low content of impurities (oxygen, nitrogen) is obtained, the resulting product is cooled, ground and subjected to the process of aluminum leaching by a known method, for example, with an aqueous solution of sodium hydroxide.

The method of obtaining an intermetallic catalyst for the oxidation of carbon monoxide and hydrocarbons was tested in laboratory conditions. Pure nickel (25...48 wt. %) and aluminum (52...75 wt. %) powders were used as starting components. The dispersion of the powders was 100...150 μm . The batch preparation scheme included dosing, mixing, filling the mold and pressing a cylindrical blank with a diameter of 20 mm and a height of 20 mm with a relative density of 0.5. The ignition of the mixture was carried out by heating to the temperature of the beginning of self-ignition. After passing through the combustion wave, exposure was carried out at a temperature of 390...460 °C for 0.5...1 hour with a gradual increase in pressing force up to 5 tons. The process was carried out in an argon atmosphere at a pressure of 1 atm. The resulting alloy was ground and a fraction of 0.5 mm was taken. The bone nickel catalyst was obtained by leaching 1 g of the obtained intermetalide at 60 °C with a 20 % aqueous solution of sodium hydroxide (100 ml) for 2 hours. Then the catalyst was thoroughly washed from traces of alkali by washing with water and ethyl alcohol.

The resulting catalyst was loaded into a plant with a flow-type reactor, and a gas consisting of a mixture of carbon monoxide, oxygen, propane, and nitrogen was passed through the plant at a temperature of 400...500 °C. The composition of the gas mixture at the reactor outlet was determined by the chromatographic method using argon or air as a carrier gas.

Based on the data of metallurgical and X-ray analysis, it was established that all the nickel in these alloys is in the $NiAl_3$ phase. In this connection, all changes in catalytic activity depend only on the state of this aluminide. Comparing the data on the activity of the catalyst with the microstructure of the starting alloys shows that the increase in activity is correlated with the grain size of the $NiAl_3$ phase. Thus, the catalyst obtained in the mode of thermal self-ignition with additional heat treatment is 1.4...1.5 times more active than the product obtained by a known method and approximately the same (10...15 μm and 15...20 μm , respectively) the sizes of the $NiAl_3$ grains in the starting alloys differ. An increase in the exposure time causes the grains of this phase to coalesce. Thus, the effect of heat treatment is reduced to a change in the quantitative ratio and grain sizes of nickel aluminides.

Changing the pressing force affects the mechanism of forming the shape and size of the pores. In the catalysts obtained by the known method, the pores have a bottle shape, and the maximum radius of their wide part is 16...25 Å (**Fig. 4.8**). Carrying out the process of pressing the product at the heat treatment stage, it was established that the catalysts are characterized by a set of cylindrical pores with a predominant radius of 30...50 Å. Micropores occupy about $\frac{1}{4}$ of the pore space. Increasing the pressing force above 5 t increases the density of catalysts, correspondingly, the degree of leaching of alloys decreases.

In order to obtain comparative data, tests of a known method of obtaining a catalyst were conducted in parallel. The catalytic activity and specific surface area of the obtained catalyst were evaluated using a known method. The resulting catalysts were used in the processes of decontamination of carbon monoxide and hydrocarbons.

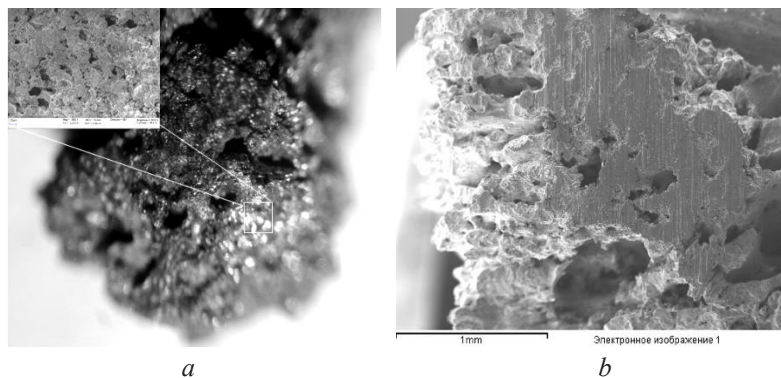


Fig. 4.8. Porous structure of the developed catalyst:
a – macrostructure, *b* – microstructure

The catalyst was loaded into a plant with a flow-type reactor. Then gas with the following composition was passed through the installation: 1,0% C_3H_8 ; 1,5% CO ; 5,8% O_2 ; 91,7% N_2 ; with a volumetric rate of 120,000 hours⁻¹ at a temperature from 100 to 400...500 °C with an interval of 50...100 °C. When using the received catalyst, the CO conversion is 100 %, and the C_3H_8 conversion is 95 %. When using a known catalyst, the conversion of CO is 85 %, and the conversion of C_3H_8 is 75 %. The specific surface area of the obtained catalyst is 81 m²/g, and for the known composition – 56 m²/g.

The analysis of the results of the comparative tests showed that the use of the developed catalyst allows obtaining a degree of purification of waste gases up to 99.9% from firing and graphitizing furnaces, and increasing the service life of the catalyst by 1.6...1.7 times. The economic effect of the introduction of the developed intermetallic catalyst is achieved due to an increase in the degree of neutralization of carbon oxide and hydrocarbons, and, as a result, a reduction in the charge for emissions of pollutants into the atmosphere.

4.4. Study of thermogravimetric indicators of cermets with an intermetallic structure

New stages of technology development and the implementation of scientific discoveries require the creation of materials that meet the increased requirements – light, high-strength, heat-resistant – such as cermets [85]. Cermets must ensure the operation of machines and devices of modern technology at elevated temperatures, voltages and speeds, as they are expected to inherit the high strength of ceramics and the viscosity of metal. Cermets are compositions of one or more ceramic phases with metals or metal alloys, possessing a complex of properties that are not characteristic of the initial components. Compositions in which the ceramic phase improves the properties of metals and alloys belong to dispersion-strengthened materials (infracermets), and compositions in which the properties of ceramics are improved by metals and alloys belong to ultracermets, example metal matrix composite [86]. Metal grains of infrared cermets contain dispersed inclusions of a ceramic phase or a needle-like ceramic phase located in neighboring grains. In ultracermets, inclusions of the metal phase are located in ceramic grains or at the junction of three grains [87]. In this regard, it is important to develop new technologies for pressure treatment of powder and composite materials, which make it possible to obtain alloys with improved physical and mechanical properties with a minimum time for their formation. Such technologies are the technology of thermochemical pressing. Thermochemical pressing is a new type of metal forming technology, in which hot products of thermochemical synthesis, which have not yet cooled down, are compacted by external force actions (pressing, extrusion, explosion processing). The grain refinement of the alloy during its synthesis under pressure occurs as a result of plastic deformation of the synthesis product and a high cooling rate. A higher efficiency of the structure grain refinement process can be achieved with plastic deformation of

the synthesized alloy during the formation of structure grains during high-temperature synthesis of the alloy under pressure. For example, by extrusion of the synthesized intermetallic γ -TiAl alloy [88].

4.4.1. TiN-Ni Systems

Cermet TiN-Ni ($NiTi$, Ni_3Ti) as the final product of the reaction is one of the research objects. The initial solid reactants for the synthesis were Ni , Ti or $NiTi$ intermetallic. The following systems of initial components $Ti + Ni + N_2$ were chosen for the synthesis of cermets [89]. Charges were prepared from titanium powders of the PTM brand and nickel of the PNE-1 brand. The reaction atmosphere of nitrogen was chosen as the synthesis atmosphere. The ratio of components was chosen based on the results of previous experiments; if the synthesis of the system was carried out for the first time, the calculation of the ratio of the mass fractions of the components was carried out according to the equations of the expected reactions with nitrogen, obtained using the THERMO and TERRA programs (Table 4.2).

Table 4.2. Results of thermodynamic analysis

Reaction equation	$T_{\text{heating}}, ^\circ\text{C}$
$0,45Ti + 0,55Ni + N_2 = TiN + Ni_3Ti$ (molten)	2356
$0,45Ti + 0,55Ni + N_2 = TiN + Ni$ (molten)	2795
$TiNi + 1/2N_2 = TiN + Ni_3Ti$ (molten)	2402
$TiNi + 1/2N_2 = TiN + Ni$ (molten)	2738

The charge prepared in this way was weighed on electronic scales, and the mixture of the selected mass was poured into the mold. A PSU-125 press was used to compact the initial blanks. The pressing pressure range was 25–120 MPa, the loading speed was manually controlled and maintained in the range of 10–50 kHz/s in order to more evenly distribute the pressing pressure over the volume of the workpiece.

The microstructures of the obtained cermets testify to different mechanisms of formation of material structures. In the first case, the process proceeds with the recrystallization of titanium nitride, the grains of which acquire a rounded shape, and the nickel with unreacted titanium dissolved in it spreads along the boundaries. In the process of recrystallization, the *Ni-Ti* solid solution forms *NiTi* intermetallic. The data of chemical analysis (Fig. 4.9, spectrum S2 and S3) made it

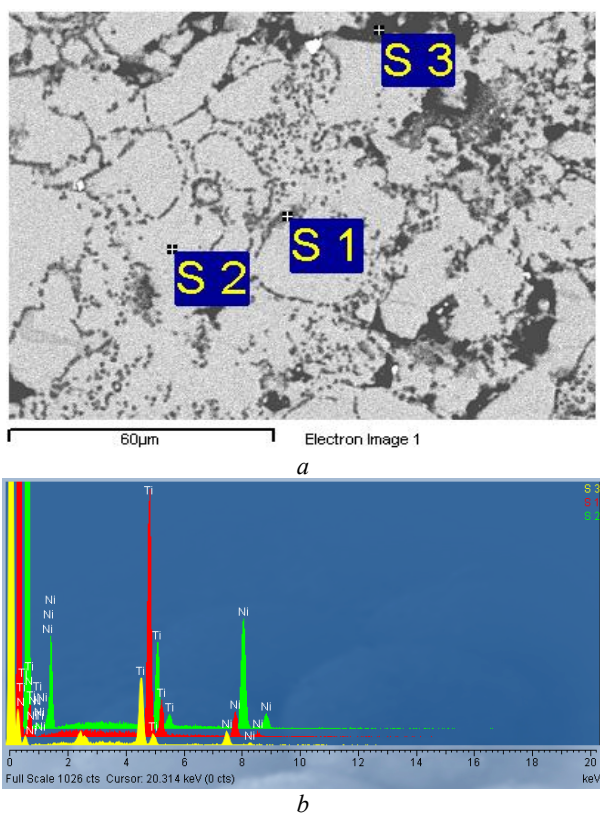


Fig. 4.9. Results of structure research *TiN-Ni* cermets:
a – microstructures, *b* – elements analyzed

possible to identify them as intermetallides containing in mass percent: S2 – 26.29 % *Ti* and 73.71 % *Ni*, S3 – 70.23 % *Ti* and 29.77 % *Ni*. This mechanism is close to the processes occurring during the sintering of titanium nitride powders with nickel [89].

As gravimetric researches have shown, cermet with this structure has high resistance to oxidation at elevated temperatures, both during rapid heating and during long exposures. When oxidized in air at a temperature of about 710 °C, the intermetallic with an exothermic effect turns into *NiTiO*₃ oxide – a compound with high resistance to long-term oxidation at temperatures above 1000 °C.

A different picture can be observed when a mixture of intermetallic and nickel powder is burned. As a result of the small value of the initial porosity and the low pressure of the reaction gas (nitrogen), a relatively slow spread of the combustion front can be observed, as well as a wide afterburning zone. In this case, a frame is formed from very small, submicron-sized particles of titanium nitride with a base of solid *Ni-Ti* solution [89].

Thermogravimetric studies showed the low resistance of this cermet to oxidation at elevated temperatures. At a temperature above 740 °C, a heat release peak is observed, which is accompanied by mass gain and is connected, as X-ray phase analysis shows, with the formation of *TiO*₂ oxide (**Fig. 4.10**). The total weight gain of the heating-cooling cycle was 7 %. When re-testing at a temperature of 905 °C, heat release is again observed, which is accompanied by a sharp increase in the weight of the sample up to 7 %.

Analyzing the results of the tests, we can say that the resistance of cermet to oxidation at elevated temperatures is completely determined by the nature of the microstructure and phase composition. Due to the intense oxidation of the titanium nitride phase at temperatures above 900 °C and the formation of an impermeable oxide film on the intermetallic surface, the most advantageous arrangement of phases from the point of view of heat resistance is a structure with

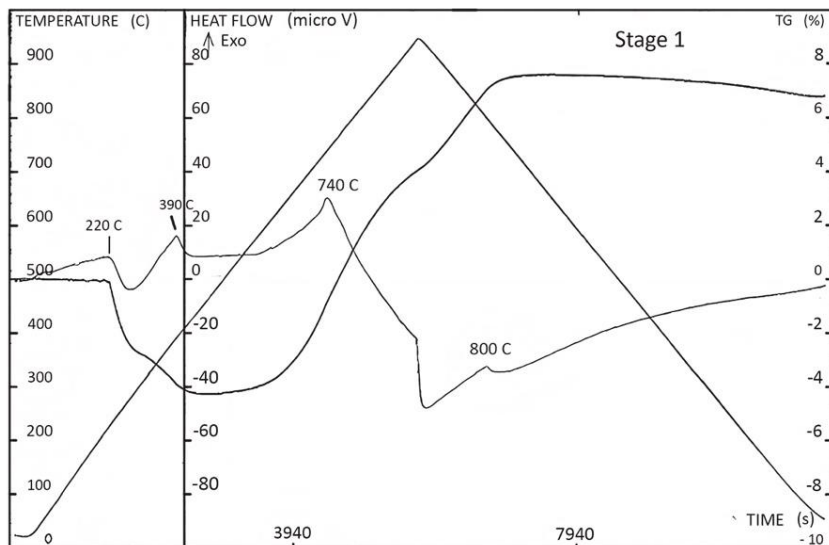


Fig. 4.10. Results of thermogravimetric studies $TiN-Ni$ cermets

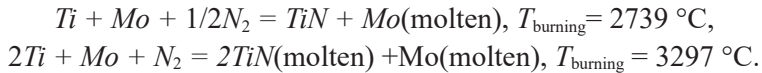
spherical particles of titanium nitride surrounded by an intermetallic phase. However, due to the extremely high temperature in the combustion front, much higher than the temperature of the reaction products, the cermet of this structure melted significantly and did not retain its shape. In case of an increase in the temperature of the combustion front due to a larger amount of solid reactant (Ti), the melting of intermediate reaction products ($TiN_{0.5}$) is observed, which impairs the permeability of the sample and causes the absence of afterburning processes, as a result of which titanium nitride remains non-stoichiometric.

4.4.2. TiN-Mo Systems

The objects of the study were *TiN-Mo* cermet, as the final product of the reaction. The following systems of initial components $Ti + Mo + N_2$ were chosen for the synthesis of cermets. Charges were prepared from titanium powders of the PTM brand, molybdenum of the MPC brand. The pressing process consists of several stages. The first stage is preparatory, where a mixture of starting powders is made into a batch briquette in a collapsible steel mold. For determination of the parameters of pressed briquettes, a nomogram was developed for determination geometric dimensions of the briquette, its mass, pressing force, amount of powder filling in depending on the ratio of the height of the briquette H to its diameter D . For the purpose of more uniform distribution of the pressing pressure according to the volume of the workpiece is held for 20 s. During the second stage, the briquette is placed in a reaction mold – a matrix for hot pressing with a heat insulator, which can be a lining heat insulator material. Combustion of the batch briquette is initiated in the mode of thermal explosion. Initiation reactions were carried out by preheating to the temperature of the beginning of spontaneous ignition. Time the passage of the combustion wave through the batch preparation corresponds to the synthesis (reaction) time $t_r = 0.5 \dots 15$ s. After the end of the synthesis, after a certain delay time of pressing, necessary for the complete the flow of thermochemical reactions and the removal of the resulting gases begins additionally pressing (compaction and plastic deformation) and holding the sample under pressure. Time exposure time is determined by the compaction time $t_k = 3 \dots 120$ s. For the next 20 min the reactor was cooled, after which the synthesized material was discharged from the matrix.

Thermodynamic analysis of thermochemical reactions of the formation of cermets according to the ratio adiabatic combustion temperature and melting temperature of the product formed, showed

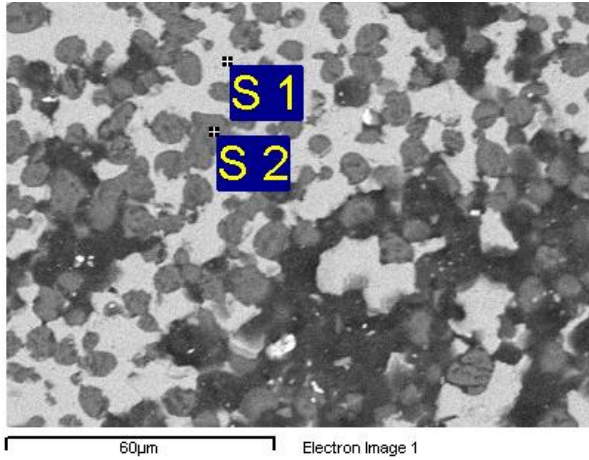
that the adiabatic combustion temperature exceeds the melting point of the product (T):



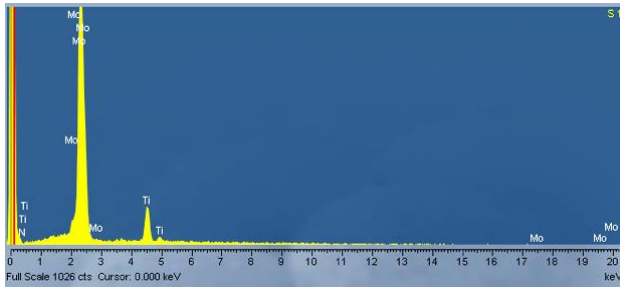
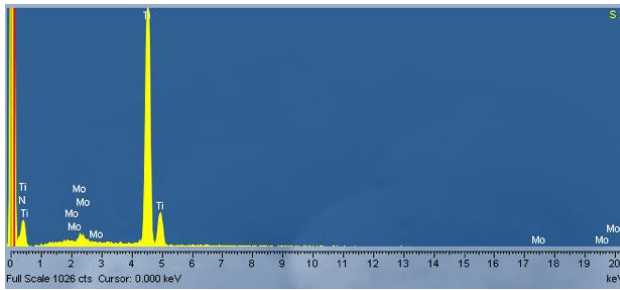
Therefore, the TiN - Mo system is characterized by interaction in the combustion mode under normal conditions ($T_0 = 298 \text{ K}$).

X-ray microspectral analysis was carried out on a SUPRA 40 WDS X-ray microanalyzer using the INKA 350 program at various points and by spectra on cross sections mounted in a special mandrel. To study the behaviour of cermets in air at elevated temperatures, model thermogravimetric studies were conducted on the TAG24 S24 SETARAM device.

The results of the microanalysis revealed more steady and finely dispersed distribution of titanium nitride compared to the $Ti + W$ system [90]. This is easily explained by referring to the results of the previous thermodynamic calculation, according to which the temperature of the combustion front is lower than the melting temperature of nitride and higher than that of molybdenum. As a result of the high velocities, the titanium that has melted in the heating zone burns, does not have time to form larger inclusions, and after interaction with nitrogen, it no longer has such an opportunity [90]. As a result, after passing the combustion front, the material is a molybdenum melt with solid particles of titanium nitride evenly distributed in it (**Fig. 4.11**). At a higher magnification in the mode of repeated electrons, it can be seen that titanium nitride particles are located around some pores, while others are inside the phase containing the metal – bond. Perhaps in the latter case, it is a closed pore formed after previous pressing, and since it did not contain enough nitrogen to form titanium nitride, titanium dissolves in molybdenum [90].



a



b

Fig. 4.11. Results of structure research *TiN-Mo* cermets:
a – microstructures, *b* – elements analyzed

X-ray phase analysis of samples synthesized under different conditions revealed another feature of this system. With an equal ratio of the nitride-forming metal (*Ti*) and the bonding metal (*Mo*), molybdenum forms compounds with nitrogen at a pressing pressure of the initial mixture above 265 kH/cm² and thereby loses its purpose of binding the ceramic phase of the element. For the $2Ti + Mo$ ratio, this threshold occurs at a much higher pressure. It is known that the compound Mo_2N at atmospheric pressure decomposes at a temperature of 1150 °C, but at elevated pressure it was obtained at 1200 °C. Therefore, the determining factor in nitriding of molybdenum is the reduced temperature at the combustion front.

Thermogravimetric study of cermets of the $TiN + Mo$ and $2TiN + Mo$ systems revealed two exothermic peaks at temperatures of 560 °C and 700 °C, which may be related to the oxidation of dissolved and connected titanium (**Fig. 4.12**). The increase in mass after a complete heating-cooling cycle at the maximum temperature of 950 °C was 5%, which is significantly less than in the $Ti + Al$ system, obtained using technologies of self-propagating high-temperature synthesis (SHS)[88].

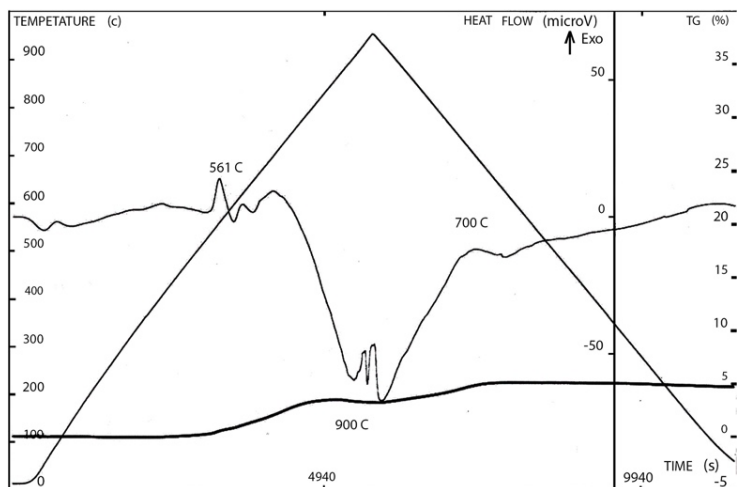
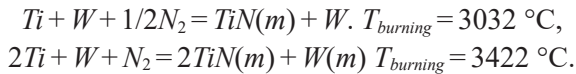


Fig. 4.12. Results of thermogravimetric studies $TiN-Mo$ cermets

4.4.3. *TiN-W Systems*

The microstructure of *TiN-W* cermet usually consists of two main components: a frame made of ceramic material *TiN* (titanium nitride) and reinforcing particles made of metallic material *W* (tungsten). The structure of *TiN-W* cermet can vary depending on the ratio of components, synthesis method and processing parameters. By optimizing TCP-process conditions and technological parameters, desired cermet properties such as hardness, strength, wear resistance and thermal stability can be achieved. In its pure state, titanium nitride (*TiN*) has a melting point of about 2950 °C, while tungsten (*W*) has a high melting point of about 3422 °C. As can be seen from the calculation of the adiabatic synthesis temperature, in the *Ti + W* system, titanium nitride will be formed in molten form, and in the case of an increase in the content of a solid combustible reagent (titanium) to 2 moles, the temperature at the combustion front is equal to the melting temperature of tungsten:



The *Ti + W* system possesses a unique attribute whereby refractory tungsten experiences contact melting at the periphery of phase separation during the formation of the primary structure. Despite the fact that the actual synthesis ends with the formation of the primary product, the evolution of the structure of this product continues even during the cooling of the samples at the pressing stage. This is facilitated by high temperature, small size of primary grains (i.e. high surface energy), presence of melts. The main processes of secondary structure formation are the growth of grains, ordering of the crystal structure, more uniform distribution of elements. The last of the mentioned processes has the greatest importance for multicomponent systems containing refractory components (*Ti*, *W*), which dissolve relatively slowly in the main phases.

Therefore, the study of the microstructure of cermets began with the analysis of images obtained using a scanning electronic microanalyzer SUPRA 40 WDS. First, a sample of the $Ti + W$ system (diameter – 30 cm) burned at a reaction gas (nitrogen) pressure of $P=100$ MPa was studied. After the previously prepared sample was placed in the working chamber of the analyzer, and the necessary vacuum was created to obtain a clear image, the search for a characteristic part of the microstructure of the sample began in the mode of reflected electrons. As a result, an area was found where two phases are clearly visible, with heavier elements having a lighter color (Fig. 4.13, *a*). In this mode, an X-ray analysis was carried out on selected points (Fig. 4.13, *b*).

The results are presented in the form of pictures of elements' distribution by sample. As expected, in the light phase there is a heavier element – tungsten, and in the darker phase – titanium and bound nitrogen. The data of spot chemical analysis (**Fig. 4.13**, spectrum S2) made it possible to identify them as titanium nitride, containing in mass percentages: S2 – 56.83 % Ti, 42.45 % N and 0.73 % W. Based on the data of the X-ray phase analysis of the powder, we can say that the sample is indeed a cermet based on titanium nitride and a tungsten bond.

At the next stage of sample investigation, the examination continued in the mode of repeated electrons. In this mode, X-ray analysis was conducted in the form of images showing the distribution of elements within the sample (**Fig. 4.14**). As anticipated, the heavier element tungsten is found in the bright phase, while titanium and nitrogen are present in the darker phase. Relying on the X-ray analysis data of the powder obtained by grinding a small portion of the sample, it can be stated that the sample indeed is a cermet based on titanium nitride and tungsten bonding.

The appearance of this microstructure, namely the shape and size of the grains, resembles the microstructure of the material formed

from the melt. Thermodynamic analysis data about temperature of the combustion front for this composition of initial solid reagents being higher than the melting temperature of the final products ($\text{TiN} + \text{W}$) confirms the conclusion that the microstructure of cermet of this composition undergoes a stage of crystallization from the melt.

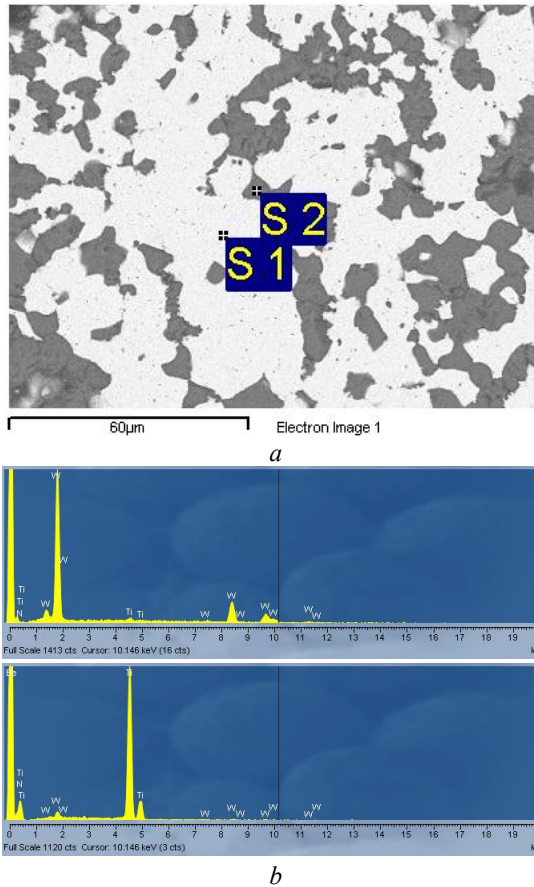


Fig. 4.13. Results of structure research $\text{TiN}-\text{W}$ cermets: *a* – elements analyzed, *b* – microstructures

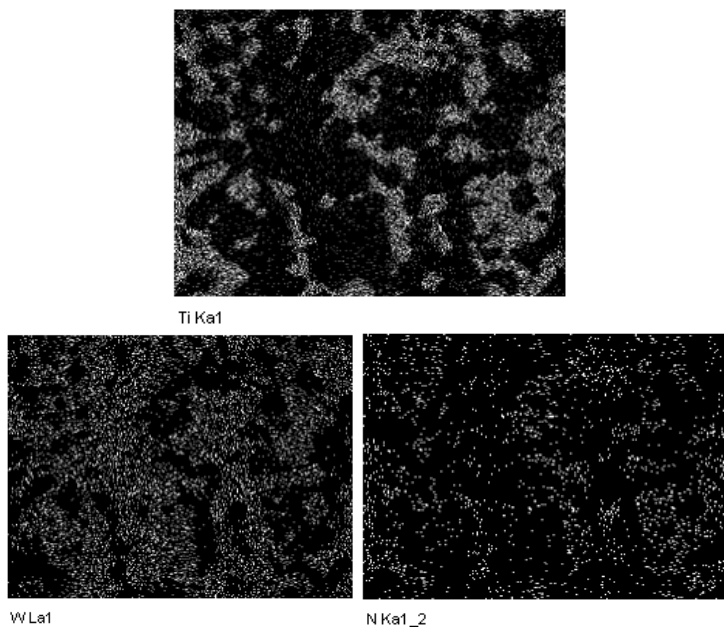


Fig. 4.14. Results of X-ray analysis of $TiN + W$ cermet

The results of the microanalysis revealed a less uniform distribution of titanium nitride compared to the $TiN-Ni$, $TiN-Mo$ and $TiCN$ -based cermets [82, 89, 90]. Investigations into the structure of the end products resulting from the synthesis of $TiN + W$ validate the assertion that the microstructure of the cermet with this composition experiences a crystallization stage originating from the molten state. Therefore, the process of secondary structure formation greatly affects the composition, shape and size of structural components. This opens up opportunities for effective management of the structure of products, since it is easier to influence the relatively slow process of secondary structure formation at the stage of thermochemical pressing, compared to the extreme process in the combustion front of high-temperature synthesis.

To investigate the performance of cermets in air at elevated temperatures, model thermogravimetric and differential thermal studies were conducted using the TAG24 S24 SETARAM device. This device is equipped with a symmetrical two-chamber furnace system, enabling the compensation of heat flows generated during heating and facilitating the measurement of sample mass changes. The heating and cooling rates ranged from 2 to 50 °C/s. Investigations have consistently demonstrated that the cermet comprising TiN and W maintains its resistance to oxidation intact even under the influence of heightened temperatures reaching 655 °C (Fig. 4.15). After undergoing a full cycle of heating and cooling, the sample exhibited a weight gain of 10%.

One notable characteristic of the titanium-tungsten system is the unique phenomenon of refractory tungsten undergoing contact melting at the boundary of phase separation within the region of primary structure formation. Investigations into the structure of the

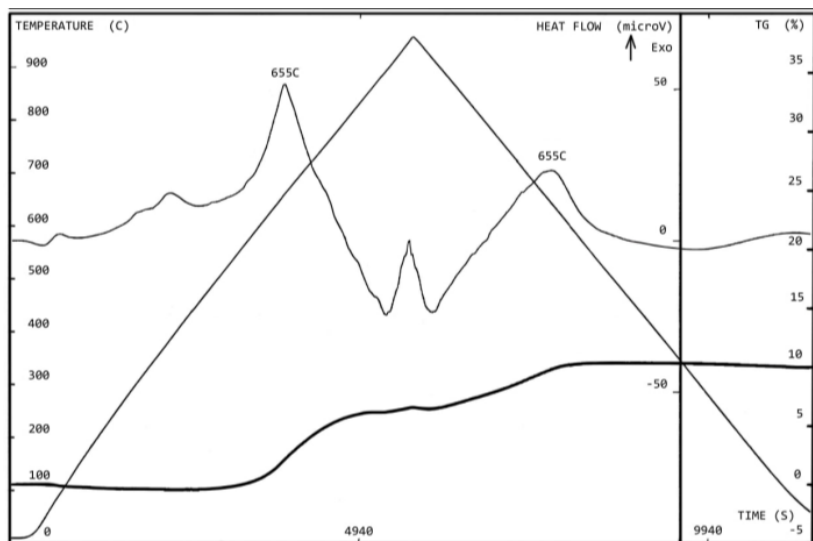


Fig. 4.15. Results of thermogravimetric studies TiN - W cermets

end products resulting from the synthesis of $TiN + W$ validate the assertion that the microstructure of the cermet with this composition experiences a crystallization stage originating from the molten state. Therefore, the process of secondary structure formation greatly affects the composition, shape and size of structural components. This opens up opportunities for effective management of the structure of products, since it is easier to influence the relatively slow process of secondary structure formation at the stage of thermochemical pressing, compared to the extreme process in the combustion front of high-temperature synthesis.