A Study of the Possibility of Obtaining Deposited Coatings based on Intermetallic Titanium and Aluminum Compounds using the Chemical Vapor Transport Method

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Abstract: - Theoretical and experimental investigations of processes of titanium–aluminum coating formation on refractory wire substrates by the Chemical Vapor Transport Reactions (CVT) method were carried out. Modelling of CVT was based on the thermodynamic analysis of an equilibrium iodide system implying the presence of one of titanium aluminides in the condensed phase, titanium and aluminum iodides in the gas phase, as well as atomic and molecular iodine. The fact that the volatility and stability of various metals are strongly interrelated was considered as a working hypothesis, which made it possible to obtain a number of alloys with the simultaneous decomposition of metal iodides constituting an alloy. Experiments on the deposition of titanium–aluminum coatings were conducted in a quasi-closed reactor, which allowed us to obtain deposited coatings on long-length refractory substrates.

1 Introduction

Titanium alloys are materials that feature the highest specific strength; they demonstrate good processing properties and high corrosion resistance. The mechanical properties of titanium are characterized by a good combination of strength and plasticity.

Titanium–aluminum alloys are materials of the highest technological and industrial importance. Aluminum is a widespread, affordable, and low-cost metal. The introduction of aluminum into commercial titanium, even in small amounts (up to 13%), makes it possible to sharply increase the heat resistance of an alloy while reducing its density and cost. This alloy is an excellent structural material. The addition of 3–8% aluminum increases the temperature of transformation of α-titanium into β-titanium. Aluminum is the only alloying stabilizer of α-titanium that increases its strength while keeping the plasticity and toughness properties of the titanium alloy constant; it also increases the heat resistance, the creep resistance, and the elastic modulus of this alloy [1].

TiAl intermetallic compounds are widely used in various fields as lightweight construction materials. With their low density, they have the advantageous properties of a high melting point, high modulus of elasticity, good antioxidant capacity, high specific strength and sufficient creep resistance at elevated temperatures [2, 3].

The Ti−Al phase diagram is characterized by the presence of wide regions of solid solutions based on α- and β-Ti and the TiAl(γ) compound.

Later studies confirmed the existence of only two compounds—Ti_3Al and $TiAl_2$—in addition to $TiAl$ and $TiAl_3$ that have already been known.

Among the intermediate phases formed in the Ti−Al system, aluminides Ti_3Al and $TiAl$ are materials of the greatest practical interest. The Ti_3Al intermetallic compound (the α_2-phase) is a superstructure based on the α-phase, in which titanium and aluminum atoms are arranged in an orderly manner. The Ti_3Al intermetallic compound has a hexagonal close-packed structure with a unit cell whose period $a\alpha$ is twice the period $a\alpha$ of the α-phase and period c is the same as that of the a-phase ($a\alpha_2 = 0.577$ nm and $c\alpha_2 = 0.462$ nm) [11].

The plasticity of the Ti_3Al intermetallic compound is negligible, which can be attributed to the peculiarities of its dislocation structure and the properties of dislocations. At room temperature, plastic deformation of the Ti_3Al intermetallic compound is mainly performed by sliding of paired superdislocations with the Burgers vector $b = a = 1/3$

<1120>. Plastic deformation of Ti$_3$Al at room temperature is limited, since dislocations $a = 1/3$ <1120> are able to slide only along the {1010} planes, and the rest of the dislocations are hardly mobile due to blocking. As a result, the number of independent planes of sliding turns out to be less than five, which does not ensure the continuity of the metal during deformation according to the Mises criterion. An unstable shear occurs in local volumes in the course of deformation, which leads to the accumulation of dislocations and the initiation of microcracks [11].

The mechanical properties of the Ti$_3$Al intermetallic compound at room temperature strongly depend on the impurity content, the microstructure type and parameters, and the micrograin size and shape. Therefore, the mechanical properties of the Ti$_3$Al intermetallic compound vary within wide limits: TS = 220−600 MPa and δ = 0−0.5%. The elastic moduli are less dependent on the above factors, and their values are: E = 140 GPa and G = 52.5 GPa. The density of the Ti$_3$Al aluminide is 4.20 g/cm^3.

As the temperature rises, the ultimate tensile strength of brittle low-strength intermetallic compound increases to about 700°C and then decreases. The ultimate tensile strength of a higher quality intermetallic compound does not experience anomalous temperature dependence. A fracture is brittle up to 600°C, so that the fracture occurs before the yield point is reached. The mobility of dislocations with Burgers vectors 1/3<1120> and 1/6<1126> increases and transverse sliding and creep of dislocations begin to develop at temperatures above 650°C, which causes the plasticity of the intermetallic compound to increase.

The creation of a fine-grained structure by applying thermomechanical treatment or powder metallurgy methods leads to a significant increase in the plasticity. The relative elongation of the fine-grain Ti$_3$Al intermetallic compound reaches 3.2% in the area of brittle fracture (at 400°C) and increases from 15 to 45% upon transition to ductile fracture (600−650°C). The Ti$_3$Al intermetallic compound with such a structure exhibits signs of superplasticity at a temperature of 1000°C and a low strain rate (σ = 120%; T = 0.46) [11].

The chemical vapor transport reactions (CVT) method [4-6] is one of the most effective methods for obtaining pure substances and coatings for various purposes for a number of branches of modern technology.

The essence of the of chemical vapor transport reactions method is in the fact that a certain substance A in a liquid or solid state interacts with gaseous substance B in a reversible reaction with the production of gaseous products, which decompose with the release of substance A in solid or liquid phase when the equilibrium conditions change after transfer to another part of the system.

The presence of a concentration gradient, along with the reversibility of the heterogeneous reaction, is a necessary condition for the transfer. A concentration gradient may occur due to a temperature difference or when the ratio of gaseous substances changes.

Substantial purification of metals from substitutional and interstitial impurities is a specific feature of transport reactions. Cleaning (refining) occurs during transfer for the following reasons:

(1) impurities do not interact with a transporting agent;

(2) impurities form nonvolatile compounds with the transporting agent;

(3) the resulting volatile impurity compounds are stable under the conditions of deposition of the refined substance;

(4) the impurity itself is volatile, and it sublimates from the sediment.

The iodide decomposition process is mainly used to obtain high-purity metals. However, the volatility and stability of iodides of various metals are strongly interrelated, which makes it possible to obtain a number of alloys with the simultaneous decomposition of metal iodides that make up the alloy. This fact is true not only for iodide, but also for other halide systems.

The following factors are indicated as necessary conditions for obtaining alloys from the gas phase using the CVT method:

(1) elimination of the conditions for obtaining a single-crystal metal;

(2) the relative volatility of iodides;

(3) the relative stability of iodides;

(4) the relative volatility of metals;

(5) the thermodynamic activity of the second components in the alloy.

In the presence of a continuous series of solid solutions, even metals that do not deposit from iodides in a free state (aluminum) can be deposited in the form of alloys.

The applicability of this method for obtaining certain substances, as well as the possibility of forming coatings with a complex composition, can
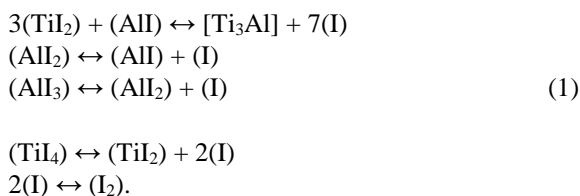
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be judged from the results of a thermodynamic analysis of the gas-phase composition. The analysis of the gas-phase composition makes it possible to determine the main transport reactions occurring in the volume, as well as to estimate the temperature parameters necessary for the transfer of the initial components with the subsequent deposition of a coating with a given composition.

2 Methods

A thermodynamic analysis of the titanium–aluminum– iodine system was carried out in order to investigate the possibility of obtaining intermetallic titanium and aluminum compounds in the condensed phase by crystallization of their iodides in the gas phase.

The main objective of the calculation was to determine the parameters of a possible process of obtaining gas-phase coatings based on intermetallic compounds: Ti_3Al and $TiAl$. For this purpose calculations of the equilibrium gas-phase composition over the Ti_3Al and $TiAl$ compounds were performed, taking into account the thermodynamic parameters of chemical compounds in a condensed phase.

Thus, a system of independent equations for the reactor volume is as follows:

$$3(TiI_2) + (AlI) \leftrightarrow [Ti_3Al] + 7(I)$$
$$(AlI_2) \leftrightarrow (AlI) + (I)$$
$$(AlI_3) \leftrightarrow (AlI_2) + (I) \qquad\qquad (1)$$

$$(TiI_4) \leftrightarrow (TiI_2) + 2(I)$$
$$2(I) \leftrightarrow (I_2).$$

All known iodides of titanium and aluminum, except TiI_3 and Al_2I_6, were taken into account in this system compiled for the Ti_3Al compound, since the results of the analysis of the titanium-iodine and aluminum-iodine systems indicate that the decomposition of these iodides occurs in the low-temperature region (up to 400°C).

A system of equations was constructed for reactions (1) based on the law of mass action that expresses the partial pressure of the iodides via the partial pressure of iodine:

$$3\ln P_{TiI2} + \ln P_{AlI} - 7\ln P_I = -20.58 + 90065/T;$$
$$\ln P_{AlI} + \ln P_I - \ln P_{AlI2} = 11.48 - 27925/T - 0.06\ln T;$$
$$\ln P_{AlI2} + \ln P_I - \ln P_{AlI3} = 19.47 - 30185/T + 0.49\ln T;$$

$$\ln P_{TiI2} + 2\ln P_I - \ln P_{TiI4} = 31.31 - 52512/T + 0.16\ln T;$$
$$\ln P_{I2} - 2\ln P_I = -8.39 - 17985/T - 0.55\ln T, \qquad (2)$$

where T (K) is the temperature, and P_i (atm) is the partial pressure of the ith component.

When considering the quality of the intermetallic compound $TiAl$ in the condensed phase, the first equation of the system (1) has the form:

$$(TiI_2) + (AlI) \leftrightarrow [TiAl] + 3(I), \qquad (3)$$
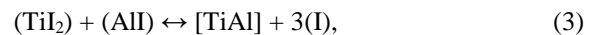
and the corresponding coupled equation of system (2) is as follows:

$$3\ln P_{TiI2} + \ln P_{AlI} - 7\ln P_I = 6.19 + 288831/T - 1.4 \ln T. \qquad (4)$$

Providing that there is no condensation of iodides and assuming the given ratio of titanium and aluminum atoms in the condensed phase, we can use the material balance equation:

$$(P_{TiI2} + P_{TiI4})/(P_{AlI} + P_{AlI2} + P_{AlI3}) = 3. \qquad (5)$$

For the system (2)–(5), it is necessary to consider the implementation of the Dalton's law:

$$P_\Sigma = P_{TiI2} + P_{TiI4} + P_{AlI} + P_{AlI2} + P_{AlI3}. \qquad (6)$$

The gas phase composition was calculated for a total pressure of 102 Pa, which corresponded approximately to the heating temperature of 40°C for the iodine evaporator. The range $T = (400–1800)°C$ is chosen as the temperature range. The results of calculations for a condensed alloy based on Ti_3Al compound are shown in Fig. 1.

Based on the results of the analysis, we can draw a conclusion that, when this model of description of CVT processes is used, the main transporting compounds in the gas phase are aluminum iodide and titanium diiodide in the temperature range of 900–1550°C and atomic iodine at temperatures above 1700°C. The reactions of formation and decomposition of titanium diiodide and aluminum iodide are the main reactions determining the process of Ti_3Al transfer. Moreover, the decomposition of these iodides should occur at temperatures not lower than 1550°C. If the condensed phase is represented by $TiAl$, the dissociation temperature of titanium diiodide and aluminum iodide increases up to 1750–1800°C.
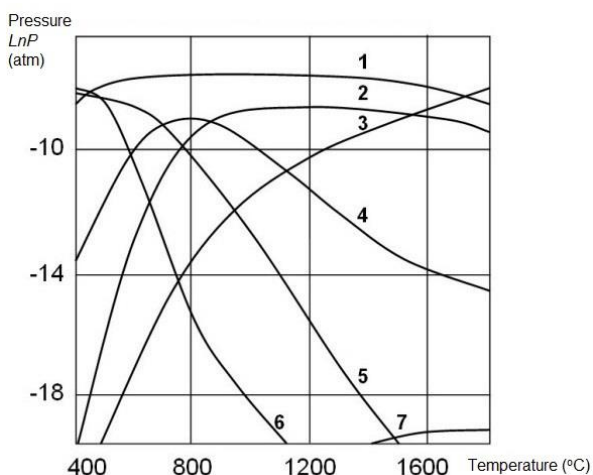
Fig. 1: The equilibrium composition of the gas phase in the titanium−aluminum−iodine system, provided that there is intermetallic compound Ti₃Al; $P_\Sigma = 102$ Pa (10^{-3} atm) in the condensed phase; $1 - TiI_2$; $2 - AlI$; $3 - I$; $4 - AlI_2$; $5 - AlI_3$; $6 - TiI_4$; and $7 - I_2$.

Experiments on the deposition of Ti₃Al and TiAl coatings were carried out using quasi-closed laboratory apparatus. Devices of this type allow the use of a moving wire as a substrate, which provides the opportunity to exercise operational control over the coating deposition process [9].

The required technological parameters of the CVT process were set up based on the results of the thermodynamic analysis of the titanium−aluminum−iodine system. These parameters included the synthesis and dissociation temperatures of volatile iodides and the total pressure in the system.

The raw material, preliminarily melted in an arc furnace, was placed in the raw area of the reactor. The growth rate of coatings at different temperature parameters of the CVT process was determined by the increase in the wire diameter for a fixed time (in a static mode or in a dynamic (on the moving wire) mode of deposition).

3 Results

Thus, the thermodynamic analysis of the titanium−aluminum−iodine system carried out in accordance with the considered model demonstrates the possibility of obtaining titanium−aluminum deposition in the condensed phase by transferring alloys based on intermetallic compounds Ti₃Al and TiAl in iodine systems.

The resulting data are in agreement with the results of the experiments. It should be noted that the

calculated temperature of synthesis (900°C) and decomposition (1550–1750°C) of iodides was higher by 100–200°C than the experimental values. This fact can be explained by the presence of errors in determining the thermodynamic functions.

The study of the appearance of the sediments has made it possible to conclude that all the samples obtained were distinguished by the high continuity and the significant degree of surface roughness. The microstructure of samples with Ti−Al coatings was characterized by the presence of a fine-crystalline sublayer and a columnar structure of the coating.
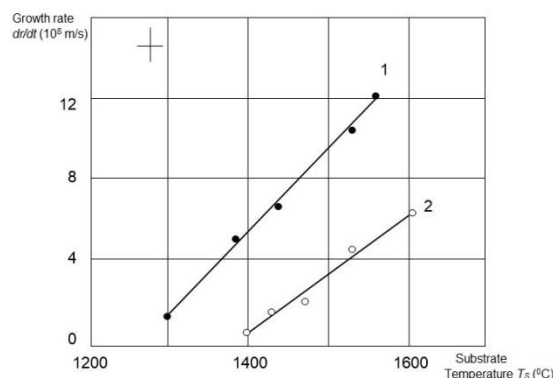

Fig. 2: The dependence of the growth rate of the titanium−aluminum coatings on the filament temperature: $T_{sublimator} = 40°C$, $T_{raw} = 900°C$; 1 – raw material of an alloy based on Ti₃Al; 2 – raw materials of an alloy based on TiAl.
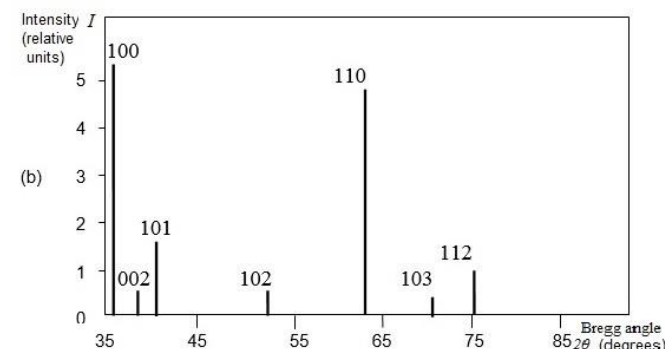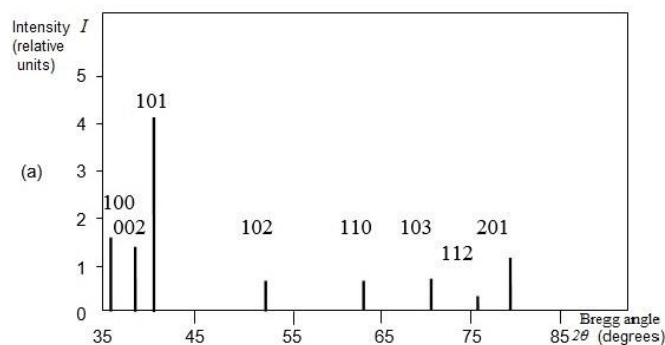

Fig. 3: The distribution of the intensities of x-ray peaks vs. the values of angle 2θ: (a) the raw alloy

based on Ti_3Al and (b) the coating obtained by transfer of the alloy based on Ti_3Al.

An increase in the deposition during the transfer of the alloy based on Ti_3Al occurred at substrate temperatures of 1300–1600°C. The dependence of the growth rate on the substrate temperature had a linear character (Fig. 2).

The increase in the temperature of the raw material from 700 to 900°C also led to the intensification of the coating-formation process. The relationship for the transfer of the alloy based on TiAl had a similar character. However, the dissociation temperature range was shifted towards higher temperatures (1400–1700°C). The growth rates of the coatings were lower compared to the results obtained for the alloy based on Ti_3Al.

4 DISCUSSION

Samples of the initial alloys and the resulting coatings were subjected to x-ray structural and phase analysis. Fig. 3 shows the intensity distributions of x-ray peaks versus the angle 2θ for the raw alloy based on Ti_3Al and for the sample with a coating deposited during transfer of this alloy. These results indicate the presence of a single-phase structure (solid solution of aluminum in α-titanium) in both raw materials and coatings.

This fact indicates that there was no ordering of the titanium−aluminum alloys with the release of the $α_2$ structure of the Mg_3Cd type under conditions of deposition of a raw alloy and deposition during the transfer of this alloy due to the short duration of these processes.

The coating is characterized by a significant increase in the intensities of the (100) and (110) lines. Therefore, we can draw a conclusion about the presence of a texture in the resulting titanium−aluminum coatings. The displacement of the deposit lines relative to the lines of the raw alloy also indicated that the aluminum concentrations in the raw materials and in the coating were different.

The presence of the disordered structure of the solid solution of aluminum in titanium both in the deposit and raw-material alloy based on Ti_3Al allowed us to estimate the compositions of the raw alloys and deposits from the results of x-ray diffraction and literature data [10].

Table I shows the dependence of the lattice parameters a and c of α-titanium on the aluminum concentration. Calculated values of the angle 2θ for the centers of gravity of lines (102), (110), (103), (200) are presented for the raw-material alloy based on Ti_3Al and for one of the samples. The titanium and aluminum concentrations determined in this way were, respectively, 76 at. % and 24 at. % for the raw material and 82 at. % and 18 at. % for the coating.

The results obtained indicate the presence of significant quantities of carbon and oxygen in the surface layers of alloys. As one moved deeper into the material, a sharp decrease in the concentration of impurity elements was observed. This was caused by refinement of the deposit in the CVT process [7, 8]. On the other hand, the surface layers of the resulting coating demonstrated a decrease in the aluminum content, which could be attributed to a change in the ratio of concentrations of Ti and Al upon their transfer to the gas phase in the CVT process.

The estimation of titanium and aluminum concentrations in the coatings obtained at different temperatures of the evaporator, raw materials, and substrate was carried out using x-ray microanalysis. The results are shown in Table II. Based on these results, we can draw a conclusion about the weak influence of the temperature parameters on the composition of deposits.

Table 1. Results of the x-ray analysis of the raw alloy and the deposit

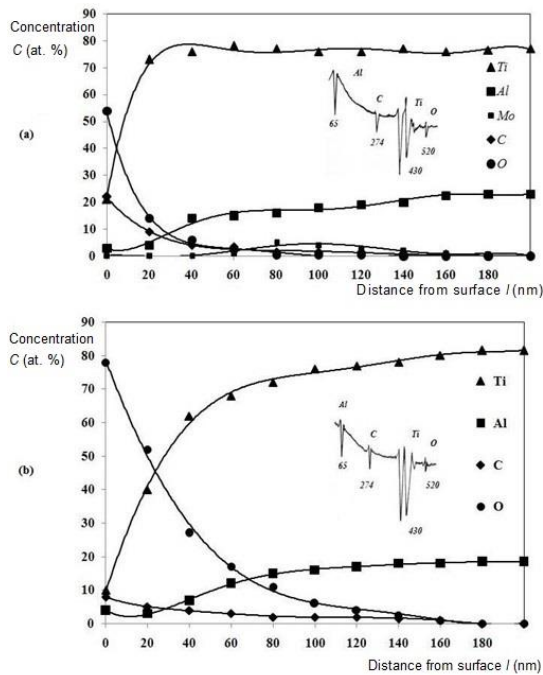| The sample	Indexes of the lines	Value of 2θ, degrees	Lattice parameters, nm	
			$a \pm \Delta a$	$c \pm \Delta c$
Raw alloy based on Ti_3Al	102	53.68	0.2900 ± 0.0003	0.4655 ± 0.0001
	110	64.17		
	103	71.47		
	200	75.77		
Cover Ti-Al; $T_{sublimator} = 40\ ^oC$, $T_{raw} = 700\ ^oC$, $T_{substrate} = 1500\ ^oC$	102	53.64	0.2909 ± 0.0003	0.4659 ± 0.0001
	110	64.06		
	103	71.38		
	200	73.77		

Fig. 4: The atomic concentration of elements in the surface layers of titanium−aluminum alloys: (a) the raw alloy based on Ti_3Al and (b) the coating obtained by transfer of the alloy, $T_{sublimator} = 40°C$, $T_{raw} = 900°C$, and $T_{wire} = 1400°C$.

The surface layers of the raw material and the deposited alloys were examined using auger electron spectroscopy. Fig. 4 shows the depth distributions of titanium, aluminum, and some impurities in the surface layers of the raw material on the basis of Ti_3Al (Fig. 4a) and the alloy coating obtained on the W−Re wire (Fig. 4b).

Table 2. The atomic concentration of the metals in the alloy coatings based on Ti_3Al and TiAl obtained at different temperature settings of the CVT process

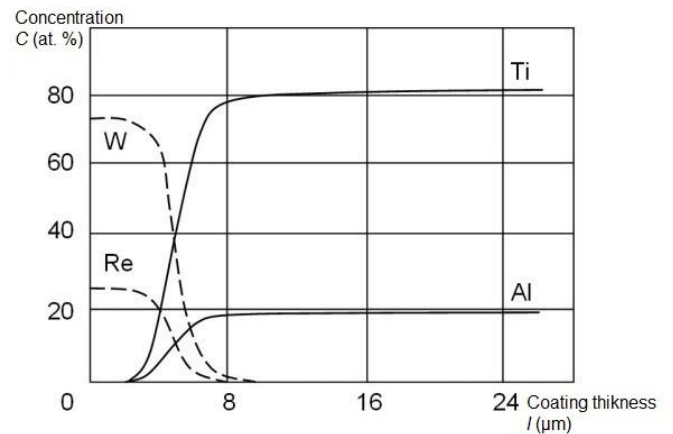| Raw materials' composition	Raw material temperature, °C	Substrate temperature, °C	Atomic concentration, %	
			Ti	Al
Alloy based on Ti_3Al	700	1420	83.9	16.1
	800	1420	82.5	17.5
	900	1420	82.9	17.1
	900	1550	83.5	16.5
	900	1380	83.7	16.3
	900	1350	81.5	18.4
Alloy based on TiAl	700	1500	75.5	24.5
	800	1500	75.2	24.8
	900	1500	74.8	25.2
	900	1400	74.5	25.5
	900	1300	75.1	24.9

Fig. 5: Distribution of elements over the thickness of the coating obtained by deposition of a Ti_3Al-based alloy from the gas phase onto the W−Re wire substrate ($T_{sublimator} = 40°C$, $T_{raw} = 900°C$, and $T_{wire} = 1400°C$).

In addition, we established the fact of a relative decrease in the aluminum concentration in the resulting coatings. Comparing the data on the aluminum concentration in the raw material alloys and the deposited alloys, we can conclude that the transfer rate of aluminum was within the range of 0.5–0.7 during the process of chemical transport of alloys based on aluminides of titanium.

Fig. 5 shows the concentration distributions of Ti and Al over the thickness of the coating obtained from the raw Ti_3Al alloy on the W−Re wire substrate with a diameter of 200 μm. The resulting coating was characterized by a high uniformity of the composition over its thickness.

5 CONCLUSION

Thus, the experimental data have confirmed the validity of the calculations for the gas-phase composition of the titanium−aluminum−iodine system, which indicate the possibility of obtaining titanium−aluminum coatings during the transfer of raw alloys based on Ti_3Al and TiAl intermetallic compounds.

The experimental values of the temperatures of dissociation of titanium and aluminum iodides are lower than the calculated ones by 100–200°C on average, which can be attributed to errors in the calculation model.

Samples were obtained that had a columnar structure and a high degree of adhesion to the substrate, with a high uniformity of the composition over its thickness.

The transfer coefficient of aluminum during the chemical transport of alloys based on titanium aluminides lies in the range of 0.5–0.7, decreasing with an increase in the aluminum content of the raw alloy.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

Anna I. Guseva was responsible for the thermodynamic calculations and statistical processing of results.

Arkady N. Silenko has organized and executed the experiments.

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