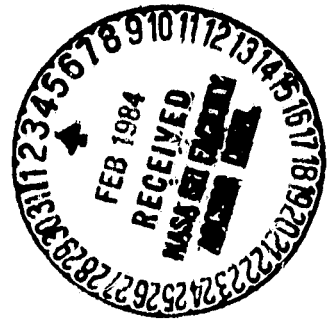


# THERMAL AND ELECTRICAL INTERACTION OF TANTALUM WITH A LOW TEMPERATURE CHEMICALLY ACTIVE PLASMA FLOW

M.V. Zake, V. E. Livepinva and
V.K. Mel'nikov

Translation of "Teplovoye i elektricheskoye vzaimodeystviye tantala s potokom nizkotemperaturnoy khimicheski aktivnoy plazmy"
Izvestiya Akademii Nauk Latviyskoy SSR, Seriya Fizicheskikh i Tekhnicheskikh Nauk, No. 2, 1980, pp 62-69

(NASA-TM-77374) THERMAL AND ELECTRICAL INTERACTION OF TANTALUM WITH A LOW TEMPERATURE CHEMICALLY ACTIVE PLASMA FLOW (National Aeronautics and Space Administration) 17 p HC A02/MF A01 CSCL 20I G3/75

N84-15980

Unclas
14504

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 DECEMBER 1983

STANDARD TITLE PAGE

| 1. Report No. NASA TM-77374 | 2. Government Accession No. | 3. Recipient's Catalog No. |
|---|---|---|
| 4. Title and Subtitle THERMAL AND ELECTRICAL INTERACTION OF TANTALUM WITH A LOW TEMPERATURE CHEMICALLY ACTIVE PLASMA FLOW | | 5. Report Date DECEMBER, 1983 |
| | | 6. Performing Organization Code |
| 7. Author(s) M.V. Zake, V.E. Liyepina and V.K. Mel'nikov | | 8. Performing Organization Report No. |
| | | 10. Work Unit No. |
| 9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108 | | 11. Contract or Grant No. NASw-3542 |
| | | 13. Type of Report and Period Covered Translation |
| 12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546 | | 14. Sponsoring Agency Code |

15. Supplementary Notes

Translation of "Teplovoye i elektricheskoye vzaimodeystviye tantala s potokom nizkotemperaturnoy khimicheski aktivnoy plazmy" Izvestiya Akademii Nauk Latviyskoy SSR, Seriya Fizicheskikh i Tekhnicheskikh Nauk, No. 2, 1980, pp 62-69
(A80-37751)

16. Abstract

The paper deals with an experimental study of radiative heat transfer and charge transfer processes from the surface of tantalum plates under conditions of unsteady high-temperature heating and oxidation. It is shown that at plate temperatures of 1800 K, the heat flux may be as high as 400 kW/sq m. Heating is shown to stimulate the emissivity of tantalum and the temperature of the free electrons which surface, through a gas boundary layer, from the plasma onto the metal.

| 17. Key Words (Selected by Author(s)) | 18. Distribution Statement |
|---|---|
| | Unclassified and Unlimited |

| 19. Security Classif. (of this report) | 20. Security Classif. (of this page) | 21. No. of Pages | 22. Price |
|---|---|---|---|
| Unclassified | Unclassified | 14 | |

# Thermal and Electrical Interaction of Tantalum with a Low Temperature Chemically Active Plasma Flow

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Refractory metals are widely used in varied technological devices: in welding units, in plasmotrons, in MHD-transformers, and so on. To provide a stable regime for industrial units in aggressive media a detailed investigation of the processes of heat and charge transfer on the surfaces of the plasma/metal interface is required. It is well known that these processes are determined by many parameters: the temperature of the gas and metal, the degree of ionization of the gas, the structure of the boundary layer, etc. A particular influence is exerted on the processes of electrical and thermal interaction of metal with a plasma flow by chemical reactions which cause a change in the physicochemical properties of the metal surface. The interconnection of thermal, electrical and chemical processes makes their comprehensive investigation necessary, with consideration of the individual properties of the metal and the plasma flow. In this work results are presented from investigation of the processes of electrical and thermal interaction of tantalum with a low-temperature plasma flow under conditions of unstable heating and oxidation. The experimental investigations were carried out on the installation described in [1]. Plates of tantalum, 7 X 6 X 1 mm, manufactured from rolled metal were used as specimens. /62*

Experimental investigations of the processes of interaction of tantalum plates with a low-temperature plasma flow were carried out at gas temperatures $T_g$ = 2500-3800 K. The rate of heating of the plates was $dT_m/dt$ = 200-300 K/s.

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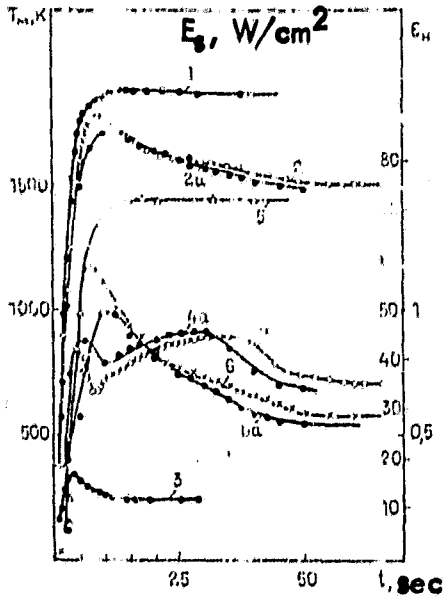


FIGURE 1. CHANGE IN TEMPERATURE (1,2), EMISSIVITY (3,4) AND HEAT LOSSES BY EMISSION (5,6) UPON UNSTABLE HEATING (1,3,5) AND OXIDATION (2,4,6) OF TANTALUM: 1-6 - $T_g$ = 3500 K; 2a-6a - $T_g$ = 3300 K.

The investigations demonstrated that heating of tantalum plates in an argon plasma is accompanied by constant change in the intensiveness of the internal integral emission of the metal, the magnitude of which is a function of the temperature and emissivity of the metal (Fig. 1). The emissivity of tantalum plates is also /63
a function of its temperature. It was established that emissivity increases upon heating tantalum in the low temperature range - from $T_m$ = 500 to $T_m$ = 1200 K - from $\varepsilon_I$ = 0.2 to $\varepsilon_I$ = 0.35 and at $T_m$ = 500 to $T_m$ = 1200-1300 K it reaches its maximum value. Upon a further increase in the temperature of the metal the values of emissivity of tantalum plates decreased on the average to $\varepsilon_I$ = 0.25-0.35. In the case of repeated heating of tantalum plates in an inert medium, the formation of a peak on the curve $\varepsilon_I$ = f(t) was not observed.

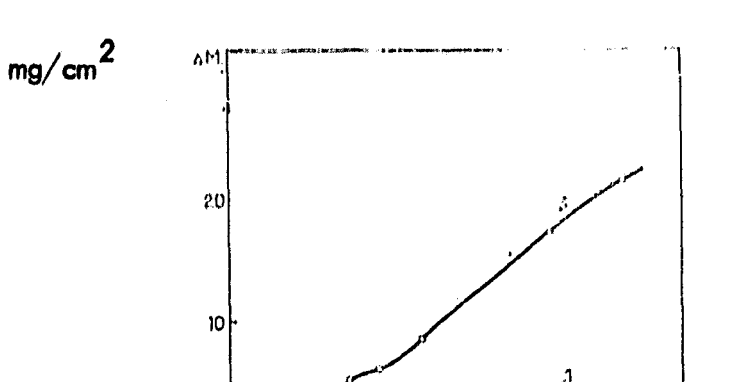


FIGURE 2. CHANGE IN INCREASE IN MASS OF SPECIMEN DURING OXIDATION OF TANTALUM GIVEN VARIOUS PLATE TEMPERATURES: 1 - $T_m$=1450 K; 2 - $T_m$ = 1490 K; 3 - $T_m$ = 1650 K.

Heating of tantalum by a flow consisting of a mixture of argon with the addition of oxygen is accompanied by a change in the kinetics of heating of tantalum plates, and also by a change in the growth kinetics of heat loss by emission and the emissivity kinetics of the metal. These phenomena are evoked largely by changes in the structure and chemical composition of the surface layer of the tantalum plates. It should be pointed out that upon heting of tantalum in an oxidizing medium two processes occur simultaneously: the formation of a solid oxygen solution in the metal, and the growth of an oxide film on the surface of the metal. The process of formation of an oxygen solution in the tantalum is characterized by the foramtion of a saturation sector on the curves of increase in specimen mass [2], and the process of oxidation by a linear course of change in curves $\Delta m=f(t)$. Experimental investigations of the kinetics of increase in mass of the tantalum specimen showed that at the initial stages of oxidation and at $T_m < 1500$ K the dominant process is the formation of a solid solution of oxygen in tantalum and on the curves of increase in specimen mass the formation of a sector of saturation is observed

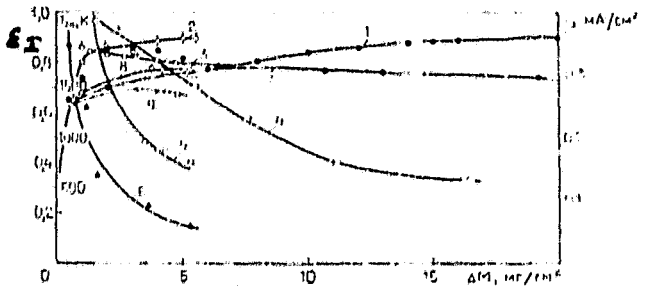

FIGURE 3. CHANGE IN VALUES OF EMISSIVITY OF TANTALUM (1 - 3), DENSITY OF REVERSE CURRENT (4 - 6) AND PLATE TEMPERATURE ( 7 - 9) ON INCREASE IN MASS OF SAMPLE DURING ITS OXIDATION PROCESS

(Fig. 2). With increased temperature of the metal plates ($T_m > 1500$ K) the saturation sector on the curves $\Delta m=f(t)$ shifts to the sector of linear growth in specimen mass, which is accompanied by an intensive increase in scale on the surface of the tantalum. At low temperatures of the tantalum plates, when dissolution of oxygen in the metal prevails ($T_m<1500$ K), the main product of the chemical interaction of oxygen with the surface of the tantalum is a low-temperature modification of the oxide $\beta$-$Ta_2O_5$; however, at $T_m>1500$ K a film of high-temperature modification of the oxide $\alpha$-$Ta_2O_5$ begins to grow.

The chemical interaction of oxygen with the surface of tantalum and the formation of an oxide film on its surface leads to a change in the kinetics of heating of the specimen; on the curves of $T_m=f(t)$ a temperature peak forms, which corresponds to a duration of heating and oxidation of the metal of 10-12 s. Further heating of tantalum and growth of the oxide film on its surface is accompanied by a reduction in the temperature of the specimen proportional to the increase in its mass (Fig. 3). Simultaneously with the change in the kinetics of heating of the tantalum plates in the process of its oxidation, a considerable change in the kinetics of growth in heat losses to emission and the kinetics of emissivity of tantalum is also observed. The emissivity of the /64
tantalum changes particularly sharply at the initial stages of heating and oxidation of tantalum, when the process of dissolution of oxygen in the metal and the formation of a film of $\beta$-$Ta_2O_5$ on the surface of the tantalum predominates. With this the values of $\varepsilon_I$ increase sharply from $\varepsilon_I$ = 0.2-0.3 to $\varepsilon_I$ = 0.85-0.9 and reach their maximum value when the duration of oxidation is t = 5 s, when the temperature of the metal plates reaches the temperature of the phase transition $\beta$-$Ta_2O_5 \rightarrow \alpha$-$Ta_2O_5$. In the region of the phase transition a decrease in the values of $\varepsilon_I$ to $\varepsilon_I$ =0.7-0.8 is observed. The onset of the process of linear oxidation of tantalum and the for tion of a high-temperature derivative of $\alpha$-$Ta_2O_5$ lead again to growth in the values of emissivity of the

metal surface to $\varepsilon_I = 0.9$ (Fig. 1). It should be noted that long-term heating of the oxidized surface $t > 30$-40 s leads to change in the kinetics of oxidation of the metal: a reduction is observed in the growth in specimen mass with a subsequent decrease in the kinetics of emissivity of the surface; the values of $\varepsilon_I$ decrease on the average to $\varepsilon_I = 0.65$-0.7, taking on a fixed value at duration of heating and oxidation of tantalum of 50-60 s. Stabilization of the emissive characteristics of the surface also leads to stabilization of the specimen temperature (Fig. 1). The characteristics of change in the emissivity of the tantalum surface in the process of its oxidation are similar in nature to change in the emissivity of titanium and zirconium plates in the process of oxidation [3]. From this analogy of the curves of $\varepsilon_I = f(t)$ it follows that the nature of change in $\varepsilon_I$ established in the process of heating and oxidation of tantalum is also connected with the interference of irradiation of the oxide film and base.

The electrical interaction of tantalum plates with a low-temperature plasma flow is determined not only by the temperature and state of the metal surface, but also by the electrophysical parameters of the stream -the temperature $T_e$ and concentration $n_e$ of free electrons, and also by the distribution of parameters in the boundary layer of the metal. Measurements of values of $T_e$ and $n_e$ which were made by the probe method and compared with the data of microwave measurements [4] showed that the electrical processes on the surfaces of the plasma/metal interface occur in the presence of a considerable lack of equilibrium, i.e., $T_e > T_g$, and the values of $n_e$ exceed the equilibrium values of the concentration of free electrons, which are calculated according to Sachs' formula [4]. The temperature of the electrons in the measurement zone is $T_e = 1.5$-1.8 eV, and the concentration of free electrons is $n_e = 10^9$-$10^{11}$ cm$^{-3}$.

The electrical interaction of argon plasma with the surface of the metal under these conditions in the absence of external

fields is accompanied by charging of the metal; as the result of the /65
fact that the thermal speed of the electrons is greater than the velocity of the ions, the metal plates acquire a floating potential, with the formation of a negative charge at the surface of the plates. In the plasma near the surface of the metal a space charge of positively charged particles - argon ions - forms. The thickness of the charged layer is equivalent to Debye length. Assessments show that under the conditions of our experiment Debye length $h_D$ is considerably less than the thickness of the dimensions of the thermal boundary layer $\delta_T$, which forms near the cold surface of the metal ($h_D=2\cdot10^{-3}$cm, $_T$=0.2 cm). Consequently, the electrons of the plasma arriving from the volume of the plasma at the surface of the metal pass through the boundary layer, in which there are temperature gradients and gas particles (Fig. 4). In studies of the processes of transfer of electrical charges under conditions similar to ours, in /5-7/ it was shown that in the boundary layer of cold metal ($T_m \leq T_e, T_g$) the electrons of the plasma are cooled and arrive at the surface of the metal at a temperature lower than the temperature of the free electrons in the stream's core. The degree of cooling of the electrons in the boundary layer depends to a great extent on the degree to which the temperature profiles of the particles are filled with gas. The dependence of the temperature of free electrons on the distribution of gas parameters in the boundary layer is not observed only when the thickness of the charged layer becomes comparable to the thickness of the thermal boundary layer. The results of work /8/, which were obtained for a moving plasma at atmospheric pressure, also lead to this conclusion.

According to the data of works /5-7/, change in the temperature of free electrons in the boundary layer of plates is brought about by volumetric losses of energy of the electrons upon elastic and inelastic interactions with heavy particles, which grow with a

reduction in temperature, but with an increase in the gas density in the layer:

$$W_d = 8/3\, m_e/m_g \gamma S_{eg} v_e n_e n_g k(T_c - T_g) \qquad (1)$$

where $S_{eg}$ is the transport section of interaction of electrons with heavy particles, $n_g$ is gas density, $\gamma$ is the coefficient of inelastic losses.

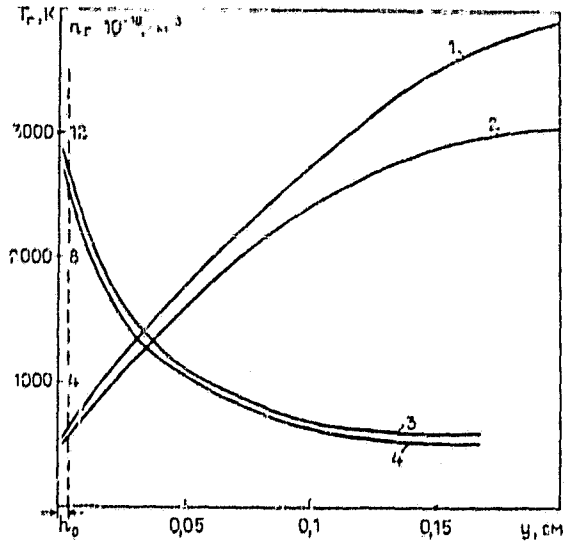


FIGURE 4. DISTRIBUTION OF TEMPERATURE (1,2) AND DENSITY (3,4) OF GAS IN BOUNDARY LAYER OF METAL: 1,3 - $T_g$ = 4000 K; 2,4 - $T_g$ = 3000 K.

From expression (1) it follows that maximum value of energy loss of free electrons in the boundary layer is achieved in the case of a cold plate; however, flattening the temperature profiles and the concentration of gas particles upon heating the metal plates leads to reduction in the extent of loss of electron energy and to growth in the temperature of the electrons arriving from the

plasma at the surface of the metal. This conclusion is confirmed /66
by the results of measurement of the dependence of $T_e$ on the temperature of the metal plates, and also by the results of investigation of the kinetics of processes of electrical interaction of an argon plasma with the metal surface during its unstable heating, which were carried out in this work. For example, the results of experimental investigation of the kinetics of the floating potential of tantalum plates, as well as of investigation of the kinetics of the electron current showed that in the absence of emission an increase in the temperature of the metal is generally accompanied by an increase in the values of the floating potential $V_f$ and in the density of the electron current (Fig. 5). The current density of ions changes negligibly when the tantalum plates are heated. From estimates of the relative increase in $V_f$ and $j_e$ it can be seen that heating of the tantalum plates has the most significant influence on the growth in values of $V_f$, the magnitude of which increases in proportion to the growth in the temperature of the electrons reaching the surface of the metal:

$$V_f \approx \frac{kT_e}{e} \ln \frac{j_e}{j_i + j_a}. \qquad (2)$$

The density of the electron current changes less significantly in the process of heating the metal; its quantity can be found, using expression /5/, in the case of a thin charged layer and given diffusion transfer of charged particles in the boundary layer:

$$j_e \approx e v_{dm} n_{em} \frac{\lambda_e}{h_D} \cdot \frac{eV}{kT_e} \cdot \left[ \frac{T_e(h_D)}{T_e(0)} \right]^{h_T} \exp \left[ - \frac{eV}{kT_e(h_D)} \frac{\ln (T(0)/T(h_D))}{1 - (T(0)/T(h_D))} \right], \qquad (3)$$

where $\lambda_e$ is the length of the free path, $n_{em}$, $v_{dm}$ are the concentration and speed of electrons near the surface of the metal.

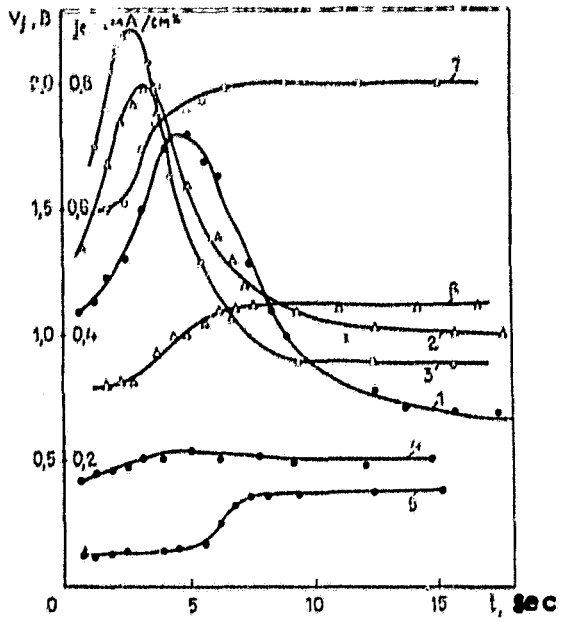


FIGURE 5. CHANGE IN THE VALUES OF FLOATING POTENTIAL (1-3), ELECTRON CURRENT DENSITY (4) AND INVERSE CURRENT (5-7) WITH UNSTABLE HEATING OF TANTALUM IN AN ARGON PLASMA: 1,4,5 - $T_g$=2800 K; 2,6 - $T_g$=3300 K; 3-7 - $T_g$=3600 K.

According to /5-7/, the energy of free electrons in the boundary layer of metal plates is lost largely due to elastic and inelastic collisions with gas particles; however, the results of the investigations in this work show that energy losses by free electrons in the boundary layer of metal may also be due to collisions of electrons with atomic metal particles, which enter the boundary layer of the plates as the result of erosion of the surface layer of the tantalum. Collisions of electons with atomic particles of gas and the corresponding metal are accompanied by excitation of the atomic particles and the arisal near the surface /67 of the plates of a glowing cloud of emissive particles. The occurrence of such luminescence is also observed upon heating and oxidation of plates of tantalum and zirconium /1/. Luminescence is more intense when the metal is first heated and decreases when it is heated repeatedly, when erosion of the metal surface layer decreases.

The kinetics of total current components and of the values of the floating potential of tantalum plates change considerably at $T_m > 1000$K, when as the result of the appearance of an emission current from the surface of the tantalum a sharp increase is observed in the inverse current density (Fig. 5). The process of electron emission is accompanied by a reduction in the values of the floating potential of the metal plates and by a negligible decrease in electron current density. The total current components and the floating potential of the tantalum plates take on fixed value at t = 15 s. When the temperature of the metal plates is increased emission current density from the surface of the metal increases sharply, and at $T_m$=1700 reaches 1.0 mA/cm$^2$. Simultaneously with the increase in the metal temperature, an increase in the work function of the emitting surface is also observed. In the range of metal temperatures from 1400 to 1700 K the work function of tantalum in an argon plasma increases from 3.4 to 4.5 eV.

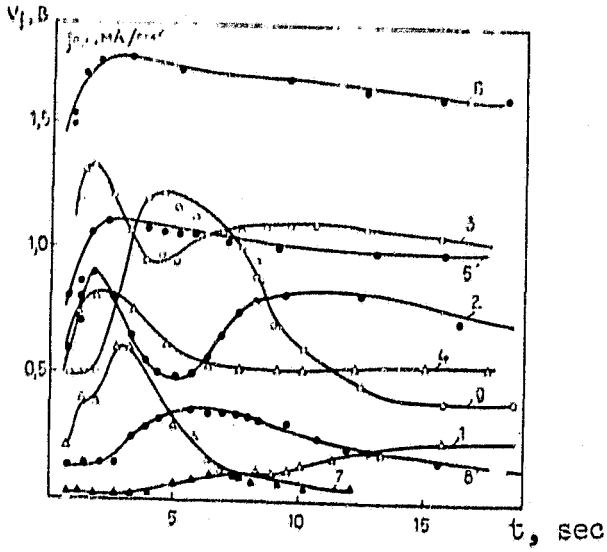


FIGURE 6. CHANGE IN VALUES OF FLOATING POTENTIAL (1-3), ELECTRON CURRENT DENSITY (4-6) AND INVERSE CURRENT (7-9) WITH UNSTABLE HEATING AND OXIDATION OF TANTALUM: 1,4,7 - $T_g$=3800 K; 2,5,8 - $T_g$ - 3300 K; 3,6,9 - $T_g$ = 3650 K.

The kinetics of the total current components and of the values of floating potential change upon addition of a small amount of oxygen to the argon flow (Fig. 6). As can be seen from the curves in Fig. 6, the presence of oxygen in the argon flux leads to a reduction both in the magnitude of the floating potential of cold metal ($T_m \approx 500$ K) and in the magnitude of the total current components - electron and ion current density. From the results of measurement of the electrophysical parameters of the stream it follows that these changes are evoked largely by change in the original parameters of the stream: reduction in temperature and concentration of free electrons. The temperature of the electrons drops by 0.2-0.3 eV on the average, but their concentration in the gas flow decreases to $10^9$ $cm^{-3}$. The change in the stream parameters revealed in the experiment does not lead to change in the mechanism of free electron transfer from the plasma to the surface of the metal, since condition $h_D \ll T$ is preserved, i.e., the predominant mechanism of transfer of free electrons from the plasma to the surface of the metal is diffusion of electrons through the boundary layer of gas, in which there are strong temperature gradients and concentrations of charged particles. As the result of preservation of the mechanism of electron transfer from the plasma to the surface of the metal, the kinetics of total current components are also maintained at the initial stages of heating of the metal (in the temperature range from 500 to 1000 K), when the chemical interaction of the metal with the plasma flow can be disregarded (Fig. 6). From the graphs in Fig. 6 it follows that heating of tantalum in this temperature range by analogy with the kinetics of the total current components and values of floating potential of tantalum upon heating in an argon medium leads to growth in the values $j_e$ and $V_f$, but ion current density remains practically unchanged. /68

Intensive chemical interaction of tantalum with oxygen begins at $T_m > 1000$K upon an increase in growth of specimen mass and change in emissivity of the metal (Fig. 1, 2). The conjunction of these processes leads to change in the kinetics of total current components

and values of $V_f$. The kinetics of inverse current - the sum of emission current and ion current densities - change most significantly as compared with the kinetics of electrical processes upon heating of tantalum in an argon medium (Fig. 6). It has been established that as tantalum is heated and oxidized inverse current density increases in a series of jumps and reaches its maximum value 5-7 sec after the plates are introduced to the plasma flow, i.e., at the moment that growth of scale ($\alpha$-$Ta_2O_5$) begins on the surface of the tantalum. Further heating and oxidation of tantalum leads to a reduction in the values of inverse current in proportion to the increase in growth of specimen mass (Fig. 3). The inverse current acquires a fixed value when the oxidation of tantalum continues for 20-25 s. It should be noted that the increase in values of inverse current at the initial stages of heating and oxidation of tantalum (to $T_m$ = 1000 K) correlates to the growth in values of emissivity of the tantalum surface and to a decrease in the values of floating potential of the plates (Fig. 6). Unlike the curves of kinetics of inverse current, for which the formation of maximum current values is revealed even at the initial stages of growth in oxide film on the surface of the tantalum, the kinetic curves of the floating potential of the plates in the process of oxidation have two peaks: a low-temperature and a high-temperature peak. The formation of a low-temperature peak on the curves $V_f=f(t)$ is due to the presence of two mutually competing processes, which lead to change in values of $V_f$: increase in the temperature of the electrons arriving at the surface of the metal during the process of its heating, and growth in the density of inverse current, the emission current (2). The appearance of a second peak on the curves $V_f=f(t)$ is due to the reduction in values of emission current upon the formation of an oxide film on the surface of the tantalum and the long-term increase in the temperature of the metal (Fig. 6). The floating potential of the tantalum plates acquires its maximum value at the moment when the specimen temperature reaches its maximum value (Fig. 6). Further oxidation of tantalum, which is accompanied by a reduction in the temperature of the metal, again leads to a reduction in the floating potential values of the plates.

In summarizing this work one can draw the following conclusions. As the result of thermal and chemical interaction of tantalum with a low-temperature plasma flow, continuous changes in the temperature and emissivity of the metal surface were observed, accompanied by changes in the electrical interaction of the metal with the plasma flow. It was established that the process of heating the metal stimulates an increase in the values of electron current density and floating potential due to an increase in the temperature of the electrons collected by the surface of the metal, and also an increase in the values of emission current and work function of the emitting surface. The chemical interaction of the metal with oxygen of the stream as the result of formation of an oxide film exerts a suppressive effect on charge transfer, reducing both the values of the total current components and the values of $V_f$ of the floating potential of the plates. These changes are evoked largely by the change in the thermal regime of the plates in the process of reaction and the formation of a protective oxide film. /69

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