Gibbs energy calculation of electrolytic plasma channel with inclusions of copper and copper oxide with Al-base

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Abstract. The oxide ceramic coating with copper inclusions was synthesized by the method of plasma electrolytic oxidation (PEO). Calculations of the Gibbs energies of reactions between the plasma channel elements with inclusions of copper and copper oxide were carried out. Two methods of forming the oxide-ceramic coatings on aluminum base in electrolytic plasma with copper inclusions were established. The first method – consist in the introduction of copper into the aluminum matrix, the second - copper oxide. During the synthesis of oxide ceramic coatings plasma channel does not react with copper and copper oxide-ceramic included in the coating. In the second case is reduction of copper oxide in interaction with elements of the plasma channel. The content of oxide-ceramic layer was investigated by X-ray and X-ray microelement analysis. The inclusions of copper, CuAl2, Cu9Al4 in the oxide-ceramic coatings were found. It was established that in the spark plasma channels alongside with the oxidation reaction occurs also the reaction aluminothermic reduction of the metal that allows us to dope the oxide-ceramic coating by metal the isobaric-isothermal potential oxidation of which is less negative than the potential of the aluminum oxide.

1. Introduction
Plasma electrolytic oxidation is used to form oxide-ceramic coatings on aluminum alloys. These coatings have a high micro-hardness, wear and corrosion resistance, dielectric properties and are applied in automotive, instrument engineering, radioelectronics, in manufacturing casings of computers and mobile phones and so on. Their synthesis, phase composition and properties have been widely studied in [1-4]. However, such coatings have certain disadvantages, in particular, high brittleness.

However it is found that oxide-ceramic coating on the copper–doped alloy D16 have better physical and mechanical characteristics [5-7]. Analysis of the microstructure of these coatings revealed the presence of copper-containing inclusions of nanometer size [5]. Conventional models, representing the processes of plasma electrolytic processing, claim that in spark channels only the reactions of oxidation of the alloying elements, available in the initial alloy, take place.

It is assumed that, alongside with the reactions of all alloy elements oxidation in the plasma channel, the secondary reactions of aluminothermic reduction of copper oxides also occur, the isobaric-isothermal oxidation potential of which is less negative than the oxidation of aluminum. Aluminothermic copper oxide reduction leads to the formation of a composite oxide-ceramic layer based on aluminium and precipitations of pure metal. Such pure metal precipitations improve the mechanical and tribological characteristics of the oxide-ceramic layers.
The purpose of this work is to substantiate by the thermodynamic calculations the possibility of the secondary aluminothermic reactions and confirm the possibility of the formation of composite oxide-ceramic layers with metal inclusions.

2. Materials and Methods

The relative stability of metal oxides at different temperatures is determined by the change in the Gibbs energy:

\[ \Delta G = \Delta H - T \cdot \Delta S \]  

(1)

where \( \Delta G \) is Gibbs energy, \( \Delta H \) is enthalpy, \( \Delta S \) is entropy, \( T \) is absolute temperature. Enthalpy \( \Delta H \) and entropy \( \Delta S \) of these substances are calculated from the equations:

\[ \Delta H_T = \Delta H_0 + \int_0^T \Delta c_p \, dT \]  

(2)

\[ \Delta S_T = \Delta S_0 + \int_0^T (\Delta c_p / T) \, dT \]  

(3)

where \( \Delta H_0 \) is standard enthalpy of substance, \( \Delta c_p \) is isobaric heat capacity, \( \Delta S_0 \) is standard entropy substance.

Consider the chemical reaction

\[ v_1A_1 + v_2A_2 + \ldots \leftrightarrow v_1'A_1' + v_2'A_2' + \ldots \]  

(4)

in which \( v_i \) is the number of moles of substance \( A_i \), involved in reaction (4) and \( v_i' \) is, accordingly, the number of moles of reaction products \( A_i' \).

The \( \Delta G \) – the Gibbs energy of chemical reaction (4) is associated with the values of Gibbs energy substances \( \Delta G \), participating in the reaction, described by equation [8]:

\[ \Delta G_i = (v_1' \Delta G(A_1', T) + v_2' \Delta G(A_2', T) + \ldots) - (v_1 \Delta G(A_1, T) + v_2 \Delta G(A_2, T) + \ldots) \]  

(5)

Enthalpy of chemical reactions \( \Delta H \) was calculated from enthalpies of reactants and reaction products \( \Delta H \) from standard elements for all substances involved in the reactions.

\[ \Delta H = (v_1' \Delta H(A_1', T) + v_2' \Delta H(A_2', T) + \ldots) - (v_1 \Delta H(A_1, T) + v_2 \Delta H(A_2, T) + \ldots) \]  

(6)

For calculations the tabulated values of Gibbs energy and enthalpy of substances formation were used [9].

3. The method of obtaining the oxide ceramic coatings

The samples of two types were manufactured for investigations. The first consisted of the copper and aluminum powders; the second – of copper oxide (CuO) and aluminum. All powders were technical pure with grains size 50 – 100 \( \mu \)m. The weight ratio of the components in the samples was 50 to 50 wt.%. The powders were mixed in a ball mill Retsh PM 100 for 40 min with velocity 100 rpm. They were compacted under pressure of 980 MPa during 12 hour. The sample size was 20 mm diameter by 4 mm height. The oxide-ceramic coating was synthesized in the electrolyte with a composition of 1 g/l KOH and 1 g/l of water glass. The current density was 30 A/dm\(^2\) for 120 min. The density ratio of the cathode and anode currents was \( I_c/I_a = 1 \). The durations of anode and cathode pulses were 6 ms. Transverse sections of the oxide-ceramic coating were prepared by the diamond polishing paper and a diamond paste. The samples were washed with distilled water and ethanol in the ultrasonic bath before examining. Their surface was examined by the scanning electron microscope EVO 40XVP with a microanalysis system INCA Energy.

The X-ray phase analysis was performed using the diffractometer DRON 3.0m (Cu-K\( \alpha \) radiation) in a step-wise mode (0.05 ° step, exposition at a point 10-15 seconds, \( 2\Theta = 20-90 \) °, the voltage at the
cathode – 30 kV, current – 10 mA). The obtained diffraction data were clarified by the Rietveld method [10] using the program package GSAS [11].

4. Results and discussion

It was found previously that in the discharge channel there were 4 regions that differed in both temperature and composition [12-16]. The temperature in the central zone of the discharge channel is 7,000 – 10,000 K and decreases to 600 K in the adjacent areas. In the discharge channel there are Al, Al$_2$O$_3$ in different states of aggregation and gaseous H$_2$O, OH, H, H$_2$, O, AlO, Al$_2$O and Al$_2$O$_2$.

The final product of the synthesis is the oxide-ceramic coating which is mainly composed of Al$_2$O$_3$.

The interactions of CuO and Cu with electrons, ions, H$_2$O, OH, H, H$_2$, and components of the electrolyte are not considered here.

Let us determine the most probable interaction of inclusions of copper and its oxide with the substances of discharge channels. We calculate the free energy (Gibbs energy) and heat (enthalpy) reactions of copper oxide CuO with aluminum using equation (5, 6):

3CuO$_{cr_{1}}$+2Al$_{cr_{1}}$ → $\alpha$-Al$_2$O$_3$$_{cr_{1}}$+3Cu$_{cr_{1}}$ (7); 3CuO$_g$+2Al$_{l}$ → $\alpha$-Al$_2$O$_3$+3Cu$_g$ (10); 3CuO$_g$+2Al$_{g}$ → $\alpha$-Al$_2$O$_3$+3Cu$_l$ (8); 3CuO$_g$+2Al$_l$ → $\alpha$-Al$_2$O$_3$+$\alpha$-Al$_2$O$_3$+3Cu$_g$ (9);

The obtained dependences are shown in figure 1 (a, b). The subscripts $g$ and $cr_{1}$ indicate the reagents in gaseous, crystalline and liquid states.

**Figure 1.** Dependence of Gibbs energy (a) and enthalpy (b) reactions on the process temperature: 1 (7); (8); (9); (10); (11).

Calculate the Gibbs energy and heat reactions of copper oxide with aluminum oxide gas (figure 2a, b):

CuO+$2$AlO → $\alpha$-Al$_2$O$_3$$+Cu_{cr_{1}}$ (12); CuO$_g$+$2$AlO → $\alpha$-Al$_2$O$_3$+$Cu_g$ (14); CuO$_{cr_{1}}$$+2$AlO → $\alpha$-Al$_2$O$_3$$+Cu_{cr_{1}}$ (13); CuO$_{cr_{1}}$$+2$AlO → $\alpha$-Al$_2$O$_3$$+Cu_{cr_{1}}$ (15).
Figure 2. Dependences of Gibbs energies (a) and enthalpy (b) of reactions on the process temperature: (12); (13); (14); (15).

The calculated free energies (Gibbs energy) and heat of reactions of oxide copper with dialuminum oxide $\text{Al}_2\text{O}$ are shown in figure 3 (a, b).

$$\begin{align*}
2\text{CuO}_{cr} + \text{Al}_2\text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + 2\text{Cu}_g \quad (16); \\
2\text{CuO}_g + \text{Al}_2\text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + 2\text{Cu}_g \quad (17); \\
2\text{CuO}_{cr} + \text{Al}_2\text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + 2\text{Cu}_{cr} \quad (18); \\
2\text{CuO}_g + \text{Al}_2\text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + 2\text{Cu}_{cr} \quad (19).
\end{align*}$$

Figure 3. Dependence of Gibbs energy $\Delta G_r$ (a) and enthalpy $\Delta H_r$ (b) of reactions on the process temperature: (16); (17); (18); (19).

Determination of the free energy and the heat reactions of oxide copper with dialuminum oxide $\text{Al}_2\text{O}$ in the presence of atomic oxygen figure 4 (a, b):

$$\begin{align*}
\text{CuO}_{cr} + \text{Al}_2\text{O} + \text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + \text{Cu}_{cr} \quad (20); \\
\text{CuO}_g + \text{Al}_2\text{O} + \text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + \text{Cu}_g \quad (21); \\
\text{CuO}_{cr} + \text{Al}_2\text{O} + \text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + \text{Cu}_g \quad (22); \\
\text{CuO}_g + \text{Al}_2\text{O} + \text{O} &\rightarrow \alpha\text{-Al}_2\text{O}_3_{cr} + \text{Cu}_g \quad (23).
\end{align*}$$
The calculated free energies and heat reactions of copper oxide with dialuminium dioxide (figure 5 (a, b)):

\[
\begin{align*}
\text{CuO}_g + \text{Al}_2\text{O}_2 & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (24); \\
\text{CuO}_g + \text{Al}_2\text{O}_2 & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (26); \\
\text{CuO}_g + \text{Al}_2\text{O}_3 + \text{Cu}_g & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (25); \\
\text{CuO}_g + \text{Al}_2\text{O}_3 + \text{Cu}_g & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (27).
\end{align*}
\]

Figure 5. Dependences of Gibbs energy (a) and enthalpy (b) of reactions on the process temperature: (24); (25); (26); (27).

The temperature dependence of the calculated free energies and heat reactions of copper oxide with aluminium in the molecular oxygen is illustrated in figure 6 (a, b).

\[
\begin{align*}
\text{CuO}_g + \text{Al}_2\text{O}_3 + \text{O}_2 & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (28); \\
\text{CuO}_g + 2\text{Al}_2\text{O}_3 + \text{O}_2 & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (29); \\
\text{CuO}_g + \text{Al}_2\text{O}_3 + \text{Cu}_g & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (30); \\
\text{CuO}_g + \text{Al}_2\text{O}_3 + \text{Cu}_g & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (31); \\
\text{CuO}_g + 2\text{Al}_2\text{O}_3 + \text{O}_2 & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (32); \\
\text{CuO}_g + 2\text{Al}_2\text{O}_3 + \text{O}_2 & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (33); \\
\text{CuO}_g + \text{Al}_2\text{O}_3 + \text{Cu}_g & \rightarrow \alpha\text{-Al}_2\text{O}_3 + \text{Cu}_g \quad (34).
\end{align*}
\]
Figure 6. Dependences of Gibbs energy (a) and enthalpy (b) of reactions on the process temperature: (28); (29); (30); (31) (32); (33); (34).

The value of the free energy and enthalpy of reactions that occur with the reagents in the gaseous state is more negative than the reaction of reagent in the solid state, and is represented correspondingly, in release of a greater amount of heat. Besides Gibbs energy for such reactions:

\[
3\text{CuO}_g + 2\text{Al}_g \rightarrow \alpha-\text{Al}_2\text{O}_3_{cr} + 3\text{Cu}_g \quad (9);
3\text{CuO}_g + 2\text{Al}_l \rightarrow \alpha-\text{Al}_2\text{O}_3_{cr} + 3\text{Cu}_g \quad (10);
3\text{CuO}_g + 2\text{Al}_l \rightarrow \alpha-\text{Al}_2\text{O}_3_{cr} + 3\text{Cu}_l \quad (11);
\]

is the lowest, what determines the priority of these reactions. Reactions involving AlO, Al_2O, Al_2O_2 take place in the final period of the plasma channel existence.

Separately the copper oxide will be reduced to copper by aluminium and will precipitate in the oxide-ceramic coating. The reverse reactions (reduction of aluminum oxide by copper) at 5000 K will not occur because of the positives values of the free energy in this temperature range.

Since in the central part of the discharge channel the temperature reaches 7000 - 10000 K, all the components are in the atomized and ionized states, and oxidizing of Al and Cu takes place in it. Reduction of copper oxide by aluminum will take place in the low-temperature areas of the discharge channel and the adjoining area.

It is possible to predict the behavior of copper and copper oxide inclusions in the aluminum matrix based on the above calculations of Gibbs energy and heat effects of interaction between the copper oxide with elements of the plasma channel and reverse reactions (interaction of copper with aluminum oxide Al_2O_3).

Contrary to the valve metals, which are characterized by the rapid oxide films formation, on the copper surface it is formed more slowly and consists of the oxides Cu (I) and Cu (II), which are semiconductors.

The breakdown of the film leads to anodic dissolution of inclusions that come out on the sample surface. This is proved by the absence of discharge channels on the surface of the compacted powder samples of aluminum and copper at first minutes of synthesis.

After dissolution of copper particles on the specimen surface spark discharges appear. Copper does not react with aluminium oxide and enters the oxide-ceramic coating in the form of metallic inclusions in figure 8 a, b.
Figure 7. SEM image of the cross-section of compacted powders of copper and aluminum. The bright areas correspond to copper (a), gray - to aluminium (b).

Spectral analysis of point 1 in figure 7a indicates that this is Cu, and point 2 in figure 7b corresponds to Al.

Figure 8. SEM image of the oxide-ceramic coating cross-section synthesized on the specimen with a mixture of compacted powders of copper and aluminium, (a, point 1)- copper, (b, point 2) – aluminium oxide.

After synthesizing the oxide ceramic coating on compacted powders of Al and Cu the coating was examined by electron microscopy. Figure 8 presents a photomicrograph of the cross-section of the oxide ceramic coating formed on a sample of compacted powders of copper and aluminum. Point 1 in figure 8 a , according to the results of spectral analysis, indicates the inclusion of Cu – 93.66 atomic% and O - 6.34 atomic%, and point 2 in Fig. 8 b Al₂O₃ with a small admixture of Cu (Al - 35.60 atomic%, O - 63.55 atomic%, Cu - 0.85 atomic%).

Unlike copper, copper oxide reacts with the active elements of the discharge channel. The aluminothermic reduction reactions of copper oxide by aluminum and incomplete oxide take place. The reaction runs with the release of large amounts of heat.

The oxide ceramic coating composition synthesized in compacted powders of copper and aluminum oxide was studied by X-ray analysis. Figure 9 shows the diffraction patterns of the initial mixture of CuO-Al (after powders milling for 40 min).
Vertical bars correspond to the location of the Bragg reflections (peaks) of constituting phases (top-down):

1 - Cu - 0.5(1) mass.% (FCC, \(a = 3.6153(8) \text{ Å}\)); 2 - Al - 44.4(2) mass.% (FCC, \(a = 4.0493(1) \text{ Å}\));
3 - CuO - 51.4(2) mass.% (monoclinic, \(a = 4.6857(3) \text{ Å}, b = 3.4256(2) \text{ Å}, c = 5.1328(3) \text{ Å}, \beta = 99.341(3)°\)); 4 - Cu\(_2\)O - 3.7(1) mass.% (cubic, \(a = 4.2692(3) \text{ Å}\))

*R*-factors (factors of discrepancy): \(R_p = 3.21\%; R_{wp} = 4.15\%\).

As has been described above, reactions of copper oxide reduction by aluminum occur with the release of a large amount of heat, which leads to the formation of the uneven surface of oxide-ceramic coating. For phase analysis the powdered oxide-ceramic coating was used. Figure 10 shows its diffraction pattern.
Vertical bars correspond to the locations of the Bragg reflections (peaks) of constituting phases (top-down):

1. Cu - 7.4(4) mass.% (FCC, \(a = 3.622(1) \, \text{Å}\))
2. CuAl\(_2\) - 8.7(9) mass.% (tetragonal, \(a = 6.067(5) \, \text{Å}, \ b = 4.877(6) \, \text{Å}\))
3. \(\alpha\)-Al\(_2\)O\(_3\) - 47.3(9) mass.% (rhombohedron, \(a = 4.765(1) \, \text{Å}, \ c = 13.009(5) \, \text{Å}\))
4. Cu\(_9\)Al\(_4\) - 36.6(5) mass.% (cubic, \(a = 2.9108(6) \, \text{Å}\)) – disordered phase

\(R\)-factors (factors of discrepancy): \(R_p = 3.47\%; \ R_{wp} = 4.61\%\).

Based on the phase composition analysis it is found that the oxide ceramic coating is composed of Cu, intermetallic compounds CuAl\(_2\), Cu\(_9\)Al\(_4\) and Al\(_2\)O\(_3\). Most likely, the intermetallic compounds are formed due to the excessive amount of Al in the discharge channels at the boundary of the oxide-ceramic coating and the compressed powder material. Unidentified peak at an angle of \(2\theta = 23.75^\circ\) corresponds to spinel AlSiO\(_2\). It is also found that the oxide-ceramic coating formed on the compacted powders of copper oxide and aluminum does not contain copper oxides. This proves our assumption about copper oxide reduction by aluminum in the discharge channels. As noted above, the reaction of copper oxide reduction by aluminum takes place with the release of a large amount of heat, which leads to the formation of the uneven surface of the oxide-ceramic coating. To form a more uniform coating it is proposed to reduce the content of CuO or introduce Cu\(_2\)O in the powder.

5. Conclusions
Calculations of Gibbs energy and enthalpy of chemical reactions between components of discharge channels and copper or copper oxide have shown the possibility of oxide-ceramic coatings alloying with copper inclusions in two ways.

1. Introduction of copper particles into the powder material, which will not interact with plasma channel and remain as inclusions.
2. Introduction of copper oxides into the powder material that will reduce in the discharge channels. The thermodynamic calculations were checked by analyzing the transverse sections of the oxide-ceramic Cu - Al coating and by X-ray analysis of CuO - Al.

The investigations of the phase composition of the oxide-ceramic coatings show the presence of copper and intermetallic materials CuAl\(_2\), Cu\(_9\)Al\(_4\) in them, thus indicating an excess of aluminum in the discharge channel.

It is established that in the spark plasma channels alongside with the oxidation reactions, the alumothermic metal reduction reactions take place and allows add in the oxide-ceramic coating with metal inclusions, the Gibbs energy oxidation of which is less negative than the aluminum oxidation.

The results of these investigations can be used for the further development of the PEO process in order to obtain new aluminum alloys for the preliminary generation of plasma spraying.
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