Work function of chemical compounds of aluminum-magnesium system

R Kh Khisamov¹, A A Kistanov², K S Nazarov¹, R U Shayakhmetov¹, G F Korznikova¹, Yu M Yumaguzin¹,³, S V Dmitriev¹,⁴, R R Mulyukov¹,³,⁴

¹ Institute for Metals Superplasticity Problems of Russian Academy of Sciences, 39 Stepan Khalturin st., Ufa, 450001, Russia
² Nano and Molecular Systems Research Unit, University of Oulu, Oulu, 90014, Finland
³ Bashkir State University, 32 Zaki Validi st., Ufa, 450076, Russia
⁴ Ufa State Petroleum Technological University, 1 Kosmonavtov st., Ufa, 450064, Russia

E-mail: andrey.kistanov@oulu.fi

Abstract. For pure metals aluminum and magnesium and for chemical compounds Al₃Mg, Al₂Mg, AlMg and AlMg₂ with crystallographic orientations (100), (110) and (111) the work function is calculated from the first principles in the framework of the density functional theory. It is shown that the dependence of the work function on the magnesium concentration in aluminium is nonlinear. The reasons for the work function differences of chemical compounds depending on the crystallographic orientation are analysed.

1. Introduction

Work function is the important emissivity characteristic for the cathodes that operate on the basis of thermionic and field emission, photo- and ion-induced electron emission phenomena. The lower work function the higher emission currents the cathode is able to produce. The emission ability of a cathode depends on the material from which it is made. For this reason, the cathode materials must have a low work function.

One of the ways to reduce the work function of the cathode is to introduce into the cathode material chemical elements with a low work function. In a rough approximation, the integral work function is the sum of the work function of chemical elements, taking into account the areas they occupy on the emitting surface of the cathode. Meanwhile, the introduced chemical elements can form chemical compounds with the cathode material, so that the work function of the compounds can be a non-additive sum relative to the work function of the cathode elements. In particular, such non-additive behavior of mechanical properties is observed in in-situ metal-matrix composites [1-6]. For a reasonable choice of the combination of chemical elements in the cathode material, it is necessary to know the work function of the cathode chemical compounds.

In this work, the work function of chemical compounds of the aluminum-magnesium system is obtained from ab initio calculations. The choice of aluminum and magnesium is associated with the fact that they are widely used as cathode materials, in particular, in glow gas discharge devices.
2. Simulation technique
The calculation of work function from the first-principles in the framework of density functional theory were performed using the plane-wave Vienna \textit{ab-initio} simulation package (VASP) \cite{7}. The first Brillouin zone was sampled with a $20 \times 20 \times 10$ k-mesh grid and the vacuum space of 15 Å was set in the direction perpendicular to the surface plane. The kinetic energy cut-off for the plane wave expansion was set to 520 eV. All the considered structures were fully optimized until the atomic forces and total energy values were smaller than $10^{-3}$ eV/Å and $10^{-8}$ eV, respectively. The work function was calculated as the minimum energy required to remove an electron from a solid to a point remote from the solid. For the calculation of work function the atomic structure (the data is taken from the open sources) of pure aluminum and magnesium as well as atomic structures of various chemical compounds of aluminum-magnesium system with crystallographic orientations (100), (110) and (111) were used (see figure 1).

![Figure 1](image)

\textbf{Figure 1.} Schematic images of atomic structure for aluminum, magnesium as well as chemical compounds of aluminum-magnesium system with different crystallographic orientations: Al (a), Al$_3$Mg (b), Al$_2$Mg (c), AlMg (d), AlMg$_3$ (f), Mg (g).

3. Results and discussion
The calculated values of the work function for pure metals aluminum and magnesium with crystallographic orientations (100), (110) and (111) are presented in Table 1. The difference of the work function of pure metals with different crystallographic orientations is related to the different crystal face structure and this is explained by the electronic smoothing effect \cite{8}. Electron gas on an atomically smooth surface creates a negative electric field, which makes it difficult for electrons to be emitted from the crystal. However, if the surface of the face is an atomically rough surface, i.e., the atoms protrude somewhat above the underlying plane of atoms, then the electron gas is redistributed in such a way that the surface becomes smooth. Electrical charge drains from the protruded atoms into cavities (underlying atomic plane). The positive charge forms on the protruded atoms while the negative charge forms on the cavities. As a result, a double electrical layer forms on the surface of a crystal face, a positively charge layer of which is directed to the vacuum. The electric field generated this way facilitates the emission of electrons from the crystal. For this reason, the work function $\phi$ of the crystal face with densely-packed atoms on the surface is higher than that of the face with the less
dense atomic surface. For example, for fcc metals the following tendency is observed: \( \phi(111) > \phi(100) > \phi(110) \) [9,10]. But for aluminum, as it was shown in experimental and theoretical works [11-14], such tendency is invalid. Our calculations showed that the (111) orientation had the lowest work function value. In the case of magnesium, the work function decreases from 3.67 eV for the (111) orientation to 3.39 eV for the (110) orientation.

The work function values for chemical compounds of the aluminum-magnesium system with different crystallographic orientations are presented in figure 2. A nonlinear decrease of the work function with an increase of magnesium concentration is observed. For the orientation (110) the work function decreases from 4.21 eV for pure aluminum to 3.74 eV for the Al\(_3\)Mg compound, then the work function increases up to 3.83 eV for the Al\(_2\)Mg compound. Further increase of the concentration of magnesium leads to a decrease of the work function to 3.39 eV that corresponds to pure magnesium. For the orientation (111) the value of the work function of the Al\(_3\)Mg compound is close that of pure aluminum which is equal to 4.20 eV. For the Al\(_2\)Mg compound the work function decreases to 3.66 eV. Further increase of the concentration of magnesium (the AlMg\(_3\) compound) the work function slightly increases to 3.76 eV, then the work function increases up to 3.39 eV that corresponds to pure magnesium. In the case of the orientation (111) the work function decreases from 4.08 eV (corresponds to pure aluminum) to 3.57 eV (Al\(_3\)Mg), then the work function increases up to 4.06 eV (Al\(_2\)Mg). After that the work function decreases to 3.29 eV that corresponds to AlMg compound. Then the work function increases to 3.8 eV for the AlMg\(_2\) compound and decreases to 3.78 eV for pure magnesium.

The differences of the work function for chemical compounds with different crystallographic orientations may be due to, firstly, the surface crystal face contains the different relation of aluminum and magnesium atoms. Secondly, the differences of the work function similarly to pure metals may arise due to the different surface atomic roughness of chemical compounds and depending on the orientations. The atomically flat surface i.e., the surface crystal face with densely packed atoms has the higher work function than the atomically rough surface i.e., the surface crystal face with the low packing atoms.

4. Summary

The work function of pure aluminum and magnesium as well as chemical compounds of aluminum-magnesium system was calculated from the first principles in the framework of the density functional theory were performed. The effect of crystallographic orientation of the free surface was studied. The work function values for aluminum with orientations (100), (110) and (111) were found to be 4.2, 4.21 and 4.08 eV, respectively. The work function values for magnesium with the same orientations were found to be 3.6, 3.39 and 3.66 eV, respectively. The nonlinear decrease of the work function of chemical compounds was observed for all considered orientations. The highest deviation from the linearly decreasing work function was observed for the orientation (100) for the chemical compound Al\(_3\)Mg (0.25 eV); for the orientation (110) for Al\(_3\)Mg (0.25 eV) and for the orientation (111) for AlMg (0.6 eV). The lowest work function, even lower than that of pure magnesium, has the AlMg

Table 1. The work function of aluminum and magnesium for different crystallographic orientations.

| Metal       | Work function in our calculations, eV | Other theoretical results of the work function, eV | Experimental results of the work function, eV |
|-------------|-------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Al (100)    | 4.20                                | 4.41[11], 4.38[12]                            | 4.41[13,14]                                   |
| Al (110)    | 4.21                                | 4.08[11], 4.30[12]                            | 4.28[11]                                     |
| Al (111)    | 4.08                                | 4.36[11], 4.25[12]                            | 4.24[13,14]                                   |
| Mg (100)    | 3.6                                 | –                                             | –                                             |
| Mg (110)    | 3.39                                | –                                             | –                                             |
| Mg (111)    | 3.67                                | 3.86[15]                                      | 3.66[13]                                     |
chemical compound with the crystallographic orientation (111) (3.29 eV). Therefore, the formation of such a chemical compound in the cathode material can increase its emissivity.

![Figure 2](image-url)

**Figure 2.** The work function calculated from the first principles in the framework of the density functional theory for chemical compounds of aluminum-magnesium system with crystallographic orientations (100) (a), (110) (b) и (111) (c).

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