Scientific Journals
Maritime University of Szczecin

Zeszyty Naukowe
Akademia Morska w Szczecinie

2014, 38(110) pp. 27–31
ISSN 1733-8670

2014, 38(110) s. 27–31

Application of the work function to study the percentage composition of aluminum alloys

Janusz Chrzanowski, Yury Kravtsov, Bohdan Bieg

Maritime University of Szczecin, Faculty of Mechanical Engineering, Department of Physics
70-500 Szczecin, ul. Wały Chrobrego 1–2, e-mail: {j.chrzanowski; y.kravtsov; b.bieg}@am.szczecin.pl

Key words: work function, shipbuilding, ionization energy

Abstract
The article uses the analytical equation for the work function of metals, made by one of the authors, to study the structure of aluminum alloys, which are increasingly used in the shipbuilding industry. For example, of selected alloys Al-Cu, Al-Ta and Al-Ti are presented graphically changes in work function depending on the percentage composition of the alloy. Also presented an equation that allows to evaluate the work function for multicomponent alloys.

Introduction

The shipbuilding sector, particularly the branch devoted to the transport of passengers on high speed ferries, is continuously overwhelmed with demands for the increase of speed and for contemporary energy spare. It is a paradox that the global market, so rich of innovative materials and technologies, gives so few suitable combinations of them for the design and production of high speed craft. So few, in fact, within such a strongly competitive market as shipbuilding is, where the costs for ship structure must be "kept as low as possible" and generally not exceed the 10% of the total price. Therefore, expensive materials and technologies are not very much appreciated by the shipbuilders.

A unique combination of properties makes aluminum one of our most versatile engineering and construction materials. A mere recital of its characteristics is impressive. It is light in mass, yet some of its alloys have strengths greater than that of structural steel. When aluminum surfaces are exposed to the atmosphere, a thin invisible oxide coating forms immediately, which protects the metal from further oxidation. This self-protecting characteristic gives aluminum its high resistance to corrosion. Unless exposed to some substance or condition that destroys this protective oxide coating, the metal remains fully protected against corrosion. Aluminum is highly resistant to weathering, even in industrial atmospheres that often corrode other metals. It is also corrosion resistant to many acids. Alkalis are among the few substances that attack the oxide coating and therefore are corrosive to aluminum. Many applications require the extreme versatility which only aluminium has. Combination of properties is being put to work in new ways. strength than pure aluminium affords. This is achieved in aluminium first by the addition of the other elements to produce various alloys, which singly or in combination impart strength to the metal. Further strengthening is possible by means, which classify the alloys roughly, into two categories, non-heat treatable and heat-treatable.

Alloys are metallic materials consisting of two or more elements combined in such a way that they cannot be readily separated by physical means. More than 90% of metals are used in the form of alloys. They represent an enormous family of engineering materials that provide a wide range of products with useful properties. Each alloy is distinct from its components, and the properties of each alloy are distinct. Indeed, the purpose in forming an alloy is to provide a metallic substance with physical, mechanical and/or chemical properties and characteristics that are different from those of

its components. Moreover, these properties are influenced by the manner in which the alloy is formed and treated. The physical and chemical properties of an alloy can be modified by heat treatment and mechanical working. In most cases, the alloy is chemically more stable than the component elements, so that alloys are designed for specific resistance to actions such as corrosion, wheater, fatigue and temperature. Other alloys are made to impart magnetic or electrical properties, strength and formability.

Aluminium alloys play an important role in many sectors of present shipbuilding. Many pleasure boats and large yachts are made of aluminium, either entirely or partially (superstructures, deckhouses, funnels, masts, etc.). Several minor, light and fast vessels, having customs, police or coast guard patrolling purposes, are aluminium ones. The material is used currently in the offshore field for the construction of specific portions of oil platforms: that is the case of living quarters and landing pads, generally made of extruded profiles. As regards civil ships, aluminium superstructures are widely used for cruise vessels, due to the need for light, efficient structures with reduced impact on vessel stability.

The general outline has shown aluminum alloys as the best technical choice for the construction of ship structures with particular speed requisites. There are also other light materials suitable for minor ships, specially mass-produced ones, such as various kinds of titanium alloys, but they are very expensive and do not ensure high productivity. Aluminum alloys own a lot of characteristics that are very interesting for high speed craft designers and builders: lightness, good corrosion resistance, good attitude to welding, cutting and shaping, in other words an excellent predisposition towards manufacturing technologies.

The work function of metals

The work function, the minimum energy required to remove an electron from the highest filled level in the Fermi distribution of a solid so that it is stationary to the point in a field-free zone just outside the solid, at absolute zero, is the most fundamental material parameter in the surface science. It plays a key role, for example, in the photo-electric effect, one of the first phenomena through which quantum mechanics unveiled itself. The work function is the result of a complex interplay between quantum mechanics and forces on the atomic scale.

The complexity of the theoretical description and the comparison of calculation results for the work function with the experimental values result from the small relative changes in the experimentally observed work function for a large number of metals. On the other hand, the experimental values for a given metal may significantly depend on the method of measurement. Generally there are four basic applied experimental methods for measuring the work function. They are based on the photoelectric effect, thermionic current, field emission and contact potential difference (CPD). For example, for potassium work function measured on the basis of the photoelectric effect is 2.3 eV while the measurement with the CPD gives 2.01 eV, respectively. These are important differences that may consequently lead to serious doubts to the meaning of the results obtained theoretically. Fundamental, theoretical studies of surface properties of metals (including work function) were initiated by Lang and Kohn [1, 2] with pioneering jellium calculations based on the local density approximation. These model calculations were later improved, and consequently could explain the basic trends exhibited by the WF in the case of simple metals, although there were still large discrepancies between theory and experiment.

In the second half of the last century the ab initio calculations of work function have been performed only in particular cases because of the large computer resources required. Nevertheless, Skriver and Rosengaard [3, 4] using the linear-response theory and linearized version of the Dyson equation improved the self-consistent Green's – function technique and were able to cut considerably the number of iterations and in result obtain about 15% conformity with the experiment for many metals.

At present the Density Functional Theory [5, 6] (DFT) is a well-established method for first principles calculations that has been remarkably successful when modeling various properties of solid state systems. DFT is the most widely used computational method because of its accuracy and reliability at a reasonable computational cost. The use of such quantum-mechanical computations is for studying materials today reached a sufficient level of accuracy where it can not only explain experiments, but also predict the properties of the systems are still immeasurable. This success is owing to significant advances in available computational power and efficient simulation software development.

In contrast to other work in this paper are not used any advanced computer programs. Work function is calculated directly from the equation introduced in paper [7] as a generalization of the first approximation presented in paper [8] where there are not additional parameters introduced by the

author. According to [7] the electron work function W is related to the Fourier transform of electron potential energy on the Fermi surface – what is compatible with the very definition of the work function.

$$W = \frac{4\pi n e^2}{k_F^2 + k_s^2} \tag{1}$$

Here: n – electron density, k_F – Fermi radius, k_s – screening parameter connected by a simple relation with the ionization energy ε_i:

$$\varepsilon_i = \frac{4\pi n e^2}{k_s^2} \tag{2}$$

Taking into account the last relation and well known expression for Fermi radius [9] we can transform equation (1) into:

$$W = \frac{\varepsilon_i}{1 + \frac{\varepsilon_i}{4e^2}\sqrt[3]{\frac{9\pi}{n}}} \tag{3}$$

Now we obtain excellent compatibility with the experiment and the average difference, between theoretical and experimental values of work function does not exceed a few percent for all metals. For example the results in terms of alkali metals are presented in the table 1, and compared with the most known (Kohn-Sham) [10] and the best (Pedrev) [11], (Skriever-Rosengaard) [4].

Table 1. The values of work function; W_{exp} – experimental values [12], W_{KS} – from Kohn-Sham calculation [10], W_P – J.P. Perdew [11], W_{SR} – H.R Skriver and N.M. Rosengaard[4], W – directly from eq. (3)

Metal	**Li**	**Na**	**K**	**Rb**	**Cs**
W_{exp} [eV]	**2.93**	**2.75**	**2.30**	**2.16**	**2.14**
W_{KS} [eV]	2.24	3.03	2.40	2.43	2.43
W_P [eV]	2.91–3.01	2.58–2.75	2.21–2.37	2.12–2.38	2.01–2.17
W_{SR} [eV]	3.15–3.33	2.76–2.94	2.34–2.41	2.22–2.32	2.03–2.13
W [eV]	**3.01**	**2.69**	**2.24**	**2.11**	**2.05**

Note, that the WF obtained directly from the equation (3) are in better of conformity with the experiment than those obtained by the Kohn-Sham calculations, and even more they demonstrate the trend of the WF for the alkali metals: greatest value for Li and the smallest for Cs. On the other hand, the values obtained by Perdew and Rosengaard are the result of complex numerical calculations and require sophisticated computer programs while the results presented in this paper are calculated directly from equation (3).

Determination of the work function for metal alloys

Pure metals are rarely used as construction materials because of their low strength properties. Therefore, the technical importance are metal alloys which are systems of two or more elements, in which the metallic bonding dominates. However, this does not mean, that all components of the alloy must be metal, since the characteristics of metal can also exhibit systems consisting of metallic and non-metallic elements such as C, N, B, P, and S. The latter is usually in a low concentration. Alloys are usually in the form of solid solutions, intermetallic phases or mixtures thereof. Exceptions are integrated immiscible with each other in a liquid state, such as aluminum and thallium. This occurs often in alloys where one component is a lead. Alloys usually have different properties than its components. Introduction of a small amount of the element causes a significant change in the properties of the alloy, for example: creep resistance, hardness, corrosion resistance, electrical and magnetic properties. The mechanical properties of alloys are generally better than the basic component and the melting point is usually less than the metal from which the resulting alloys.

For many reasons the knowledge of the work function of the various alloys may by very interesting. To date, there are no generally known theoretical studies showing changes in work function of the alloy according to the percentage composition of the individual metals. There are only a few works relating to experimental studies. Equation (3) can analyze the correlation for any of alloys consisting of two or more metals. For this purpose, let us consider an alloy of mass m consisting of k different metals, for which the percentage of the alloy is respectively α_k. In this arrangement, the electron gas is composed of N electrons, wherein:

$$N = \sum_k N_k Z_k \tag{4}$$

Here N_k means number of atoms of k-th metal in given mass of alloy, Z_k valence of k-th metal. Number of the metal ions in the sample we can determine from the relation:

$$N_k = \frac{m\alpha_k N_A}{M_k} \tag{5}$$

N_A is traditionally Avogadro's number, whereas M_k means atomic mass of the atom. Taking into account the relation above we can rewrite the equation (4) in form:

$$N = mN_A \sum_k \frac{\alpha_k Z_k}{M_k} \tag{6}$$

Hence the electron gas density for a given alloy is:

$$n = \frac{N}{V} = \frac{mN_A \sum_k \frac{\alpha_k Z_k}{M_k}}{V} = \rho\, N_A \sum_k \frac{\alpha_k Z_k}{M_k} \tag{7}$$

Where ρ is the alloy's density. If this value is not known it can be determined by means of simple calculations, assuming that the volume of the alloy V is the sum of its individual components volumes V_k. Because:

$$V_k = \frac{\alpha_k}{\rho_k} m \Rightarrow V = \sum_k V_k = m \sum_k \frac{\alpha_k}{\rho_k} \tag{8}$$

Eventually the density of the alloy we find from the equation:

$$\rho = \frac{1}{\sum_k \frac{\alpha_k}{\rho_k}} \tag{9}$$

As a result the electron gas density n for given alloy is given by:

$$n = N_A \frac{\sum_k \frac{\alpha_k Z_k}{M_k}}{\sum_k \frac{\alpha_k}{\rho_k}} \tag{10}$$

If we assume now that the ionization energy occurring in the equation (3) we can find from the relation:

$$\varepsilon_i = \sum_k \alpha_k \varepsilon_{ik} \tag{11}$$

We obtain the expression for the work function of the alloy in the form:

$$W = \frac{\sum_k \alpha_k \varepsilon_{ik}}{1 + \frac{\sum_k \alpha_k \varepsilon_{ik}}{4e^2} \sqrt[3]{\frac{9\pi}{n}}} \tag{12}$$

Where n is given by relation (10).

In the examples calculation, in order to simplify the notation, we confine ourselves to the two-component alloys, analyzing first the Al-Cu alloy. The relevant parameters characterizing both metals and necessary for the calculation are presented in the table 2.

For two-component alloy relation (10) simplifies to the form:

$$n = \frac{\rho_1 \rho_2}{\alpha \rho_2 + (1-\alpha)\rho_1} \frac{N_A}{M_1 M_2} \left[\alpha M_2 Z_1 + (1-\alpha) M_1 Z_2\right] \tag{13}$$

While the work function we can calculate by the formula (14).

The results of calculations are presented in the graph 4 for different percentage configurations α of copper.

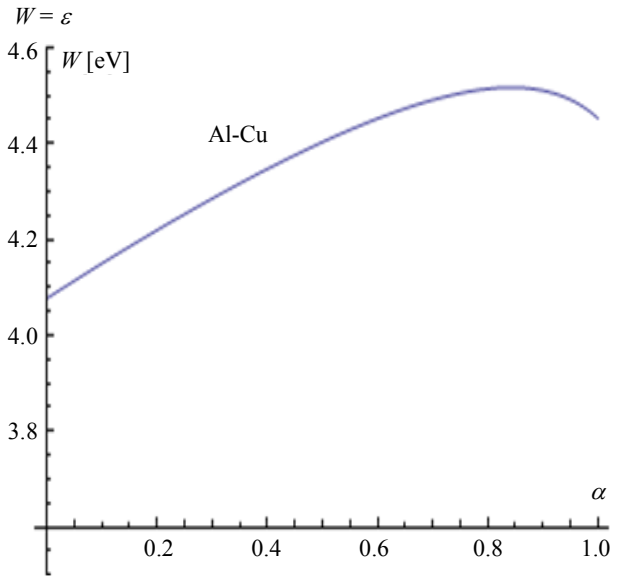

Fig. 4. Dependence of the work function Al-Cu alloy on the percentage concentration of Cu

In line with expectations for $\alpha = 0$, which corresponds to pure aluminum work function is 4.08 eV, whereas the experimental value of the work function of aluminum is 4.1 eV. For $\alpha = 1$, pure copper, the work function is 4.45 eV, experimental value of the work function for copper is 4.51 eV. Increasing the percentage of copper in the alloy makes also clear increase in work function – almost linear relationship. Note the characteristic peak, where the work function of the alloy is significantly higher than the work function of copper. Similar behavior we can observe for other aluminum alloys figures 5 and 6.

$$W = \frac{\alpha\varepsilon_{i1} + (1-\alpha)\varepsilon_{i2}}{1 + \frac{3^{2/3}\pi^{1/3}\left(\alpha\varepsilon_{i1} + (1-\alpha)\varepsilon_{i2}\right)\left(\frac{M_1 M_2\left((1-\alpha)\rho_1 + \alpha\rho_2\right)}{N_A\left(\alpha M_2 Z_1 + (1-\alpha) M_1 Z_2\right)\rho_1\rho_2}\right)^{1/3}}{4e^2}} \tag{14}$$

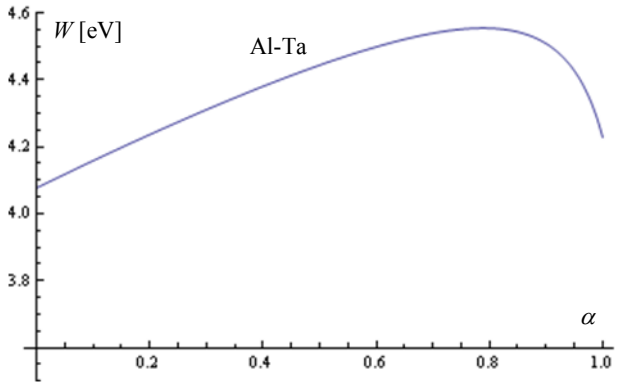

Fig. 5. Dependence of the work function Al-Ta alloy on the percentage concentration of Ta

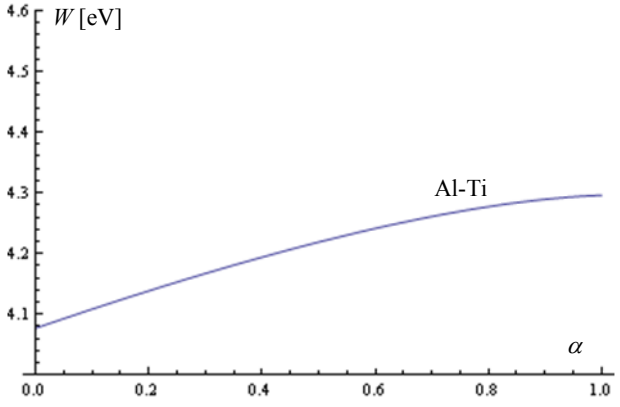

Fig. 6. Dependence of the work function Al-Ti alloy on the percentage concentration of Ti

Table 2. Parameters aluminum and metals used in alloys

Metal	Density [g/cm^3]	Atomic mass [g]	Ionization energy [eV]	Work function [eV]
Aluminum	2.70	26.981	6.01	4.10
Cooper	8.95	63.546	7.75	4.51
Thalium	16.65	180.950	7.91	4.15
Titanium	4.50	47.880	6.85	4.30

In the same way we can determine the value of the work function for any alloy consisting of two or more metals.

Conclusions

Because of the lack of reliable experimental data we limited ourselves to the simplest model, assuming a significant restrictions in the form of the relation (8) and (9). The density of the alloy may depend on the method of obtaining a given sample, so a simple ratio 7 need not be true in any situation. And the seemingly logical assumptions about the ionization energy – equation (11), after long reflection may be also questionable. However, all these and many other doubts about the structure of the alloys can be better explained using the work function and presented in this paper equations.

References

1. N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).
2. N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).
3. H. L. Skriver and N. M. Rosengaard, Phys. Rev. B 43, 9538(1991).
4. H. L. Skriver and N. M. Rosengaard, Phys. Rev. B 46, 7157(1992).
5. P. Hohenberg; W. Kohn, Phys. Rev. B 1964.
6. W. Kohn, Rev. Mod. Phys. 1999, 71, 1253 (Nobel Lecture).
7. J. Chrzanowski, Chinese Physics B (2013).
8. J.Chrzanowski, Yu.A. Kravtsov, Physics Letters A 375, 671-675. (2011).
9. N.W. Ashcroft, N.D Mermin: Solid State Physics. New York. Holt, Rinehart and Winston (1976).
10. W. Kohn, L.J. Sham, Phys. Rev. 140, A1133 (1965).
11. J.P. Perdew, H.Q. Tran, E.D. Smith, Phys. Rev. B, 42, 11627(1990).
12. Periodic Table of Elements (EnvironmentalChemistry.com).