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Study of Fe-W-Cr and Ni-Cr-W Systems for the Development of High-Quality Anti-Diffusion Coatings

A theoretical study of Fe-W-Cr and Ni-Cr-W metal systems as bases for anti-diffusion coatings in thermoelements is presented. Using the calculation of dissociation energies, the stability of the components and their ability to form effective barrier layers are assessed. The constructed graphs of the dependence of the dissociation energy on the interatomic distances make it possible to predict the optimal ratios of components to increase diffusion stability.

Keywords: semiconductor, thermoelectric materials, nanostructure, solid solutions, tellurides, n- p-types, resistance, contact, chemical bond, binary compounds, theoretical models, quantum patterns, electron density, state diagrams.

Introduction

Anti-diffusion coatings are a key element in creating highly efficient thermoelectric energy converters, as they provide thermal and structural stability at elevated temperatures and prevent the diffusion of atoms between semiconductor legs and metal electrodes [1]. The most critical factor is the mutual diffusion of atoms at the “thermoelectric material – metal contact” interface, which leads to the formation of intermetallics, an increase in resistance, and degradation of the module. In this case, special attention should be paid to undesirable electrical and thermal resistances, since their significant increase can reduce the maximum energy efficiency of cooling and generator converters made of Bi_2Te_3-based materials [2]. To prevent these processes, anti-diffusion barrier layers and interconnect structures optimized in composition and properties are used [3]. Multicomponent systems based on Fe, Ni, Cr and W [4, 5, 6, 7] are promising, providing a combination of high electrical conductivity with increased

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diffusion and thermomechanical stability. Theoretical simulation, including the calculation of dissociation energies, electron density, and quantum patterns, allows predicting the phase stability and properties of coatings at the design stage. Construction of phase diagrams and analysis of the interaction of components in such systems make it possible to optimize the composition to obtain coatings with increased diffusion resistance and contact reliability [8, 9].

The Fe-W-Cr and Ni-Cr-W metal systems have the potential to create such coatings due to their ability to form strong chemical bonds, stable solid solutions, and barrier layers that prevent interdiffusion of atoms [10, 11, 12]. Binary and ternary compounds in these systems exhibit high dissociation energies, which provides increased thermal stability and reliability of contacts in the material structure.

The purpose of this work is a theoretical study of Fe-W-Cr and Ni-Cr-W systems for the development of high-quality antidiffusion coatings by calculating dissociation energies depending on interatomic distances.

Theoretical models of chemical bonding of Fe-W-Cr and Ni-Cr-W systems

Within the framework of the theoretical analysis of the processes of formation of antidiffusion barriers based on Fe-W-Cr and Ni-Cr-W, the theory of interatomic interaction was revised. Based on the crystal chemical approach generalized for the description of electronic configurations, the concept of effective ionic radii R_{Un} was introduced and the relationship between them and the number of electrons on the outer shell of the atom was established through a system of auxiliary equations:

$$\lg R_{UA}^{x} = \lg R_{UA}^{0} - x\,\mathrm{tg}\alpha, \tag{1}$$

where $R_{U\mathrm{A}}^{0}$ is the radius of atom A in the unexcited state, and x is valence.

Since, according to the crystal chemical approach, equation (1) describes the change in R_U of both A and B atoms with a change in the number of electrons in the orbitals of which, then dependence (1) takes the form of a system of equations:

$$\lg R_{UA}^{+x} = \lg R_{UA}^{0} - x\,\mathrm{tg}\alpha_{\mathrm{A}}, \tag{2}$$

$$\lg R_{U\mathrm{B}}^{-x} = \lg R_{U\mathrm{B}}^{0} + x\,\mathrm{tg}\alpha_{\mathrm{B}}, \tag{3}$$

$$d_1 = R_{UA}^{+x} + R_{U\mathrm{B}}^{-x}, \tag{4}$$

where d_1 is the internuclear distance *A–B*.

A disadvantage of the crystal chemical approach is the presence of a minimum interatomic distance d_{min} which is justified by the increase in the internuclear distance with a change in ionicity between the same atoms. However, in many cases the internuclear distances *A–B* in compounds and alloys are less than the value d_{min}. Further development of the model was focused on overcoming the limitations of the crystal chemical approach by translating it into the language of quantum chemistry. It should be taken into account that during bond formation, the spherical symmetry of the electron density of A and B atoms is broken and is accompanied by a redistribution of electrons to other directions of interatomic interaction.

This condition is fulfilled if the removal $(+\Delta e)$ of electrons or their localization $(-\Delta e)$ change the values of the charges that a given pair has at $d_1 = d_{min}$, i.e. $Z_{ef}A(B) =$

$Z_{min}A(B) + \left(\frac{\Delta l}{2}\right)$ and are described by the system of equations:

$$d_1 = R_{UA}^{ZA} + R_{\mathrm{UB}}^{ZB}, \tag{5}$$

$$\lg R_{UA}^{ZA} = \lg R_{UA}^{0} - (Z_{minA} + \tfrac{\Delta e}{2})\mathrm{tg}\alpha_{\mathrm{A}}, \tag{6}$$

$$\lg R_{\mathrm{UB}}^{ZB} = \lg R_{\mathrm{UB}}^{0} - (Z_{minB} + \tfrac{\Delta e}{2})\mathrm{tg}\alpha_{B} \tag{7}$$

Replacing x in the system of equations (2)–(4) by $(Z_{min} + \frac{\Delta e}{2})$ in (5)–(7) changes the physical meaning of these equations. The function $d_1 = f(Z_{ef})$ is calculated from the standpoint of the crystal chemical approach, $(Z_A = -Z_{\mathrm{B}})$ is correct from a quantum point of view only when $d_1 = d_{min}$, but this is sufficient for system (5)–(7) to be solved for a known d_1 and the effective radii and redistribution of electron density to be found for all possible values of d_1 in the compounds under study. Thus, taking into consideration the quantum interpretation of the empirical material made it possible to obtain an expression for the energy of chemical bonds in the form:

$$D_{A-B}^{i} = \left(\frac{C_1(R_{UA}^{0} + R_{UB}^{0})}{(\mathrm{tg}\,\alpha_A + \mathrm{tg}\,\alpha_B)}\right)\left(\frac{C_2 d_i}{d_i^2 - R_{UA}R_{UB}} - \frac{1}{d_i}\right), \tag{8}$$

where $R_{UA(B)}^{0}$, $tg\alpha_{\mathrm{A(B)}}$ are the coefficients of equations (2)–(4) for A and B atoms; R_{UA} and R_{UB} are the effective radii of their ions in bonds (A–B) of length d_i; i is the number of non-equivalent interatomic distances in compounds under consideration; C_1 is the coefficient reflecting the relationship between the dimensional and energy characteristics of the interatomic interaction (measured in electron volts); C_2 is the coefficient depending on the type of crystal structure and chemical bond and is chosen to be dimensionless.

The given equation (8) was used in calculating the dissociation energies of nonequivalent chemical bonds of the ternary systems Fe-W-Cr and Ni-Cr-W. The dissociation energies for the nearest neighbors at different interatomic distances d_{i} $(1 \le i \le 11)$ of structural modifications of iron, nickel, chromium and tungsten are given in Tables 1 and 2.

Table 1

Dissociation energies D_i of Fe-W-Cr system depending on interatomic distances d_i

d_i(Å)	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
Fe-Fe D_i (eV)	1.915	1.835	1.768	1.704	1.646	1.591	1.54	1.491	1.446	1.363	1.424
Cr-Cr D_i (eV)	2.586	2.487	2.394	2.309	2.229	2.155	2.085	2.0202	1.96	1.901	1.929
W-W D_i (eV)	3.5723	3.435	3.308	3.19	3.08	2.98	2.907	2.79	2.706	2.627	2.552
Cr-W D_i (eV)	3.014	2.896	2.791	2.691	2.598	2.513	2.452	2.355	2.284	2.216	2.155
Fe-W D_i (eV)	2.674	2.571	2.487	2.39	2.316	2.228	2.171	2.088	2.019	1.97	1.909
Fe-Cr D_i (eV)	2.2	2.11	2.036	1.964	1.896	1.833	1.79	1.718	1.67	1.617	1.571

The high strength of W-W, Fe-W, and Cr-W bonds indicates the key role of tungsten in the formation of structural elements resistant to thermal and diffusion processes.

As in the previous system, tungsten significantly increases the bond energy. The W-Ni bond is stronger than Cr-Ni bond, indicating a more effective contribution of tungsten to the strength of the interatomic interaction with nickel.

Table 2

Dissociation energies $D(\varphi_i)$ of Ni-Cr-W system depending on interatomic distances d_i

d_i(Å)	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5
Ni-Ni D_i (eV)	1.574	1.514	1.458	1.406	1.361	1.312	1.27	1.23	1.1925	1.157	1.1245
Ni-Cr D_i (eV)	1.9578	1.883	1.813	1.778	1.688	1.6316	1.593	1.53	1.483	1.439	1.399
Ni-W D_i (eV)	3.544	3.408	3.275	3.165	3.051	2.954	2.886	2.766	2.683	2.607	2.533

Based on the calculation results obtained in Tables 1 and 2, the dependences of dissociation energy on the interatomic distance were constructed for Fe-W-Cr (Fig. 1) and Ni-Cr-W (Fig. 2) systems.

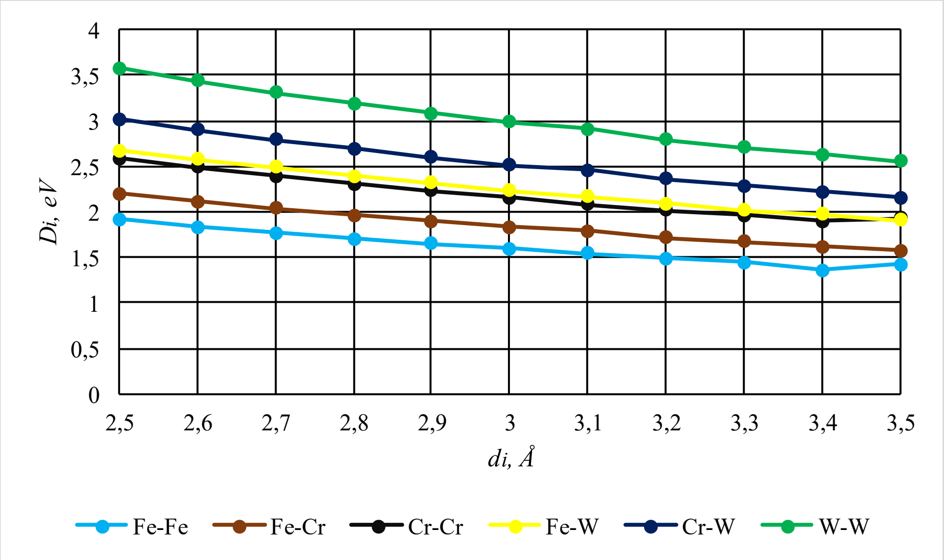

Fig. 1. Dissociation energies D_i of Fe-W-Cr system depending on interatomic distances d_i

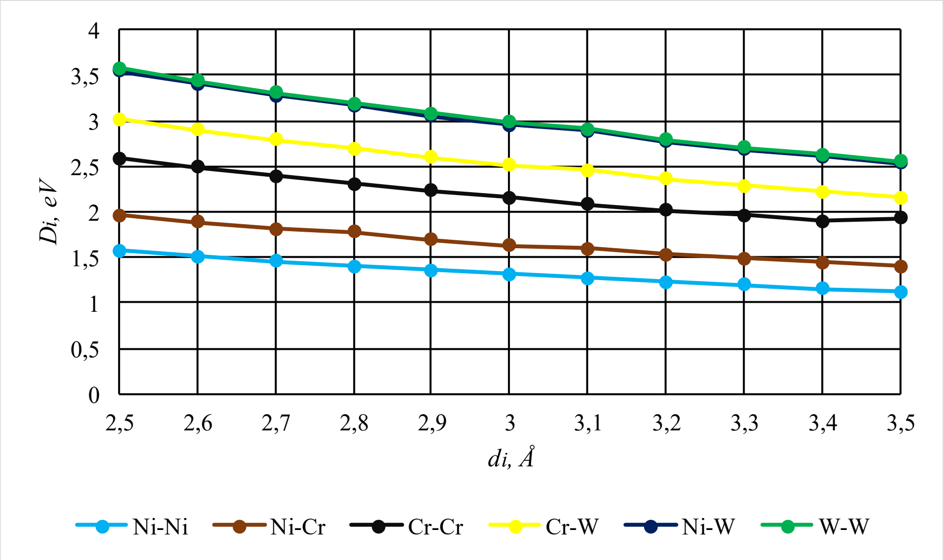

Fig. 2. Dissociation energies D_i of Ni-Cr-W system depending on interatomic distances d_i

The visual representation confirms the general trend of decreasing bond strength with increasing interatomic distance.

Conclusions

The use of a crystal chemical approach with the interpretation of quantum chemistry made it possible to calculate the dissociation energies D_i of chemical bonds in Fe-W-Cr and Ni-Cr-W systems, which is crucial for assessing the strength of bonds in alloys. The calculations confirmed the inverse dependence of the dissociation energy on the interatomic distance for all types of bonds. It was found that tungsten forms the most energetically strong bonds (W-W, Ni-W), which demonstrate the highest D_i values compared to other components (Fe-Fe, Ni-Ni, Cr-Cr, Fe-Cr, Ni-Cr). The high dissociation energy of bonds involving tungsten is a theoretical justification for its key role in creating high-quality anti-diffusion coatings.

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Дослідження систем Fe-W-Cr та Ni-Cr-W для розробки антидифузійних покриттів підвищеної якості

Представлено теоретичне дослідження металевих систем Fe-W-Cr та Ni-Cr-W як основи для антидифузійних покриттів в термоелементах. За допомогою розрахунку енергій дисоціації оцінено стабільність компонентів і їх здатність формувати ефективні бар'єрні шари. Побудовані графіки залежності енергії дисоціації від міжатомних відстаней дозволяють прогнозувати оптимальні співвідношення компонентів для підвищення дифузійної стійкості.

Ключові слова: напівпровідник, термоелектричні матеріали, наноструктура, тверді розчини, телуриди, n- p- типи, опір, контакт, хімічний зв'язок, бінарні сполуки, теоретичні моделі, квантові закономірності, електронна густина, діаграми стану.

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