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PHASE BOUNDARIES AND INTERFACIAL ENERGY IN QUASIBINARY BORIDE AND METAL CERAMIC EUTECTIC SYSTEMS

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The a priori pseudopotential method is employed to propose a model by which phase boundaries form in quasibinary eutectic systems. Interfacial energy for boride and cermet quasibinary eutectic composites, LaB_6–TiB_2 and LaB_6–ZrB_2, is calculated for different temperatures.

Keywords*: eutectic, phase boundary, interfacial energy, a priori pseudopotential.*

INTRODUCTION

Interactions between atoms at the interface of eutectic phases are studied in the papers [1, 2]. The energy states of the atoms in boundary layers and inside eutectic phases significantly differ. Computational experiments confirm that the eutectic is not a mechanical mixture of the phases but a single system of interacting phases.

Regular interface of the eutectic phases is associated with the minimum energy between components, i.e., interfacial energy. The minimum interfacial energy is reached when a combination of symmetry, orientation, and lattice parameters corresponds to the greatest number of atomic matches [3]. The interface means a transition zone separating two phases or components that are insoluble in each other [4].

The eutectic solidified in normal conditions has an interface of about 1 $m^2 \times 1$ cm^3 [4]. The extremely large interface resulting from solidification is indicative of eutectic compositions and predetermines their specific properties.

To determine the interfacial characteristics, various theories can be applied: macroscopic (for example, thermodynamics gives average interfacial characteristics); atomistic, allowing conclusions on the interfacial structure and development of geometric and energy models; electron, describing interactions at the boundary between eutectics in terms of quantum mechanics [4, 5].

There is currently no comprehensive description of all interfacial phenomena in eutectic composites. In this regard, it is difficult to provide their comprehensive overview. Moreover, most studies address intergranular boundaries or outer surfaces of the samples [4, 5]. Being so important for eutectic materials, the phase boundaries are just starting to receive researchers' attention. As pointed out in [5], there are no experimental data for heterogeneous interface. For this reason, it is difficult to describe interaction between atoms through the interface, especially in case of unlike phases. The interface between two phases can be coherent or locally coherent. The local coherent regions are presented as 'cells' in [6, 7]. The notion of 'supercell' is introduced for complete description of

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the actual interface. The supercells consist of crystalline lattices of two phases and are separated by a layer of vacuum. Nevertheless, the notion of 'virtual cell' is more productive. The virtual cell is located along the interface between the components, allowing for contact of crystalline lattices forming a quasicoherent boundary. The first-principles calculations of energy in the electron–ion system of the components and the entire composite [8, 9] serves as a basis for developing a model to describe the formation of interfaces in eutectic systems.

EXPERIMENTAL PROCEDURE, CALCULATION RESULTS, AND DISCUSSION

In the LaB_6–MeB_2 system, the phases are connected at the interface through boron atoms belonging to two components. There are 0.75 LaB_6 molecule and 0.25 TiB_2B molecule at the interface in the eutectic LaB_6–TiB_2 composite. The number of boron atoms is common for the two components at the interface and amounts to five. The common atoms make the boundary strong enough. The number of common atoms depends on lattice parameters of the components. For TiB_2, ZrB_2, and HfB_2, these parameters are very close and contact energies are almost the same, which is not the case for VB_2 and CrB_2. Because of the small lattice parameter (c is the hexagonal lattice parameter of transition metal diborides), the degree of possible contact between the two components increases with higher likelihood that LaB_6 (002), (004), and MeB_2 (002) atomic planes match, leading to greater contact energy. These statements have been supported by calculations.

Since the interface is characterized by the energy of interaction between molecules (atoms) of the two phases, there is excess internal energy in the composite at the interface compared to the energies of the components. The energy of the components and system was calculated applying the pseudopotential method [8, 9]. For this purpose, we used the scheme [10], according to which the total energy of components A and B that are not in interaction becomes

$$U_1 = (C^2U_{AA} + CU_A) + ((1 - C)^2U_{BB} + CU_B). \quad (1)$$

The U_A and U_B values include the kinetic energy of free electron gas, exchange-correlation effect, and electron energy in the first-order perturbation theory by pseudopotential for respective molecules [8]; U_{AA} and U_{BB} are the energy of interaction between A–A and B–B; C is the concentration of component A.

The energy of the (A–B) system allowing for interaction between components A and B (U_{AB}) can be written as

$$U_2 = C^2U_{AA} + CU_A + (1 - C)^2U_{BB} + CU_B + 2C(1 - C)U_{AB}. \quad (2)$$

The excess energy determining the surface factor is eventually equal to

$$\Delta U = U_1 - U_2 = -2C(1 - C)\, U_{AB}. \quad (3)$$

The energy of interaction between the two components U_{AB} (calculated with the a priori pseudopotential method) can be represented as a sum of interatomic pair potentials $\Phi_{AB}(\vec{R}_{i,j})$ [8, 9]:

$$U_{AB} = \frac{1}{N}\sum_{i,j}\Phi_{AB}\left(\vec{R}_{i,j}\right), \quad (4)$$

where $\vec{R}_{i,j} = \vec{R}_i(A) - \vec{R}_j(B)$ is the distance between atoms i and j belonging to molecules A and B.

Since the energy of interaction between two molecules does not depend on the position of other molecules but is only a function of k_F (Fermi momentum) or Z/Ω [11], we used approximation for the potential of interaction between the molecules similarly to that for the atoms to calculate the energy of interaction between molecules of different types located at distance R from each other [10]:

$$\Phi_{AB}(R) \approx \left[18\pi Z_A Z_B \frac{V_A(2k_F)V_B(2k_F)}{k_F^2}\right]\frac{\cos(2k_FR)}{(2k_FR)^3}, \quad (5)$$

where Z_A, Z_B and V_A, V_B are the number of free electrons and pseudopotentials (calculated at $q = 2k_F$) for A and B. The Fermi momentum was determined through the volume and charge per molecule. In this case, the molecule

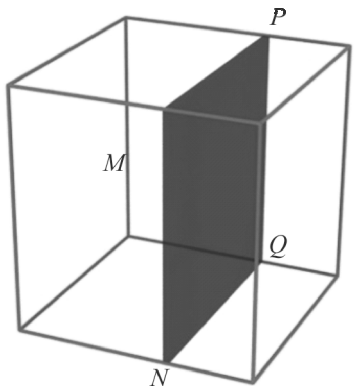

Fig. 1. Unit cell of a virtual crystal: *MNPQ* is the interface of two phases

consists of two parts at the interface: molecule A with concentration C and molecule B with concentration $(1 - C)$. The volume of this molecule is

$$\Omega = C\Omega_A + (1 - C)\Omega_B, \tag{6}$$

and the charge is

$$Z = CZ_A + (1 - C)Z_B, \tag{7}$$

where Ω_A and Ω_B are the volume of components A and B; Z_A and Z_B are the number of external elements of components A and B, respectively. The distance R between molecules was determined from the minimum of function (5) ($k_F \approx 1.09$).

To determine the contact surface of two components, we used a 'virtual cell' with volume (6) and charge (7). Figure 1 represents a cube (unit cell of a virtual crystal) and contact surface between the two components. The average interfacial area in a virtual cell can be found if we present $\Omega = A^3$ (virtual cell parameter, $A = MQ$) and then the contact surface area becomes

$$S = S_{MNPQ} = A^2. \tag{8}$$

The interfacial energy of two components per unit contact area is

$$\gamma = -U_{AB} / S, \tag{9}$$

or

$$\gamma = -U_{AB}(R) / \Omega^{2/3}. \tag{10}$$

TABLE 1. Volume (Ω), Interfacial Area (S), Molecule Interaction Energy (U_{AB}), and Interfacial Energy (γ) in Eutectic Systems

System	Ω, a.u.	S, a.u.	U_{AB}, a.u.	γ, J/m^2
LaB_6–TiB_2	406.107	54.84	0.12165	3.454
LaB_6–ZrB_2	400.980	54.12	0.12420	3.582
LaB_6–HfB_2	410.786	55.26	0.11965	3.388
LaB_6–VB_2	290.155	43.83	0.22886	8.131
LaB_6–CrB_2	338.530	48.57	0.22516	7.219
B_4C–TiB_2	576.077	69.24	0.80700	18.149
B_4C–SiC	517.210	64.50	0.77800	18.783
TiB_2–SiC	151.326	28.397	1.58000	40.050

Note: a.u.—atomic units (here and in Tables 2 and 3).

Fig. 2. Interface of LaB_6 and MeB_2 atomic planes filled with boron atoms

The results (Table 1) show that the surface contact energy is small in the LaB_6–MeB_2 system compared to the B_4C–TiB_2, B_4C–SiC, and TiB_2–SiC systems. The energy of contact between the two components is so weak in the LaB_6–MeB_2 system that it can be neglected and the composite can be regarded as a mechanical mixture, which is not the case for the TiB_2–SiC, B_4C–SiC, and B_4C–TiB_2 systems. In the TiB_2–SiC system, components contact through the TiC clusters, locally appearing at the contact surface. The contact energy is higher in this case, as confirmed by calculations.

Two phases or two components (if they are insoluble) in the quasibinary eutectic systems have different crystalline lattices and different sizes of atoms and molecules. It is rather difficult to account for these effects to determine the interfacial energy for two components in quantum mechanics calculations. To solve this issue, likely contact between crystalline structures of the components should be considered first in determining the contact surface. In the LaB_6–MeB_2 system, two components are connected through boron atoms. Base MeB_2 (002) and LaB_6 (004) surfaces are in the same plane (Fig. 2). The boundary is quasicoherent with this contact of the two

TABLE 2. Calculated Surface Areas (S) and Interfacial Energies (γ) in Eutectic Systems

System	S, a.u.	γ, J/m^2
LaB_6–TiB_2	38.03	4.928
LaB_6–ZrB_2	37.78	5.123
LaB_6–HfB_2	39.15	4.799

TABLE 3. Average Volumes and Contact Surface Energies at Different Temperatures in Virtual Crystal Approximation

T, K	LaB_6–TiB_2		LaB_6–ZrB_2	
	Ω, a.u.	γ, J/m^2	Ω, a.u.	γ, J/m^2
0	406.107	3.454	400.980	3.582
300	408.941	3.407	403.770	3.535
500	410.830	3.371	405.613	3.497
750	413.191	3.331	407.891	3.457
1000	415.670	3.290	410.222	3.416
1500	420.273	3.214	414.832	3.336
2000	424.955	3.139	419.440	3.271
2500	429.716	3.056	424.051	3.109
2750	435.011	3.010	428.360	3.106

components. Figure 2 shows the contact of boundaries with a heavy line. The distance between the boron atoms for two structures, LaB_6 and MeB_2 (Me=Ti, Zr, Hf), is almost the same.

Within one LaB_6 unit cell, the length of contact line is approximately $2d$, where $d = a\sqrt{2}/4$ is the distance between boron atoms on (004) plane in LaB_6 and a is lattice parameter. The contact area, $S = 2dc$, corresponds to the minimum contact of two borides in the eutectic system (c is the hexagonal MeB_2 lattice parameter). The unit cell volume was determined with Eq. (6) and the energy of interaction between the components U_{AB} with Eqs. (4) and (5). The results are presented in Table 2.

The two approaches differ in how the contact surface is determined. The contact surface between two components is average in the 'virtual' crystal model (Fig. 1). The contact energy is 2.44 J/m^2 at the maximum contact surface (area being formed with face diagonals). For more accurate determination of the contact surface, the ratio of cell parameters needs to be taken into account. If we consider that contacts with common boron atoms can form in the systems even when the base MeB_2 surfaces do not match the LaB_6 (001) planes, the 'virtual' cell option can be perceived as the average energy of possible contacts in the systems.

Applying the quasiharmonic approximation model proposed in [12], we calculated the interfacial energy for the systems over a range from zero to eutectic temperature. The interaction energy of the components and the volume per average molecule were obtained for each temperature. The interfacial energy at different temperatures was calculated with the respective equations. The results for the LaB_6–TiB_2 and LaB_6–ZrB_2 systems are summarized in Table 3.

CONCLUSIONS

The computational experiment for boride and metal ceramic quasibinary eutectic composites allows the following conclusion: eutectics are not a mechanical mixture of components but represent a system of interacting crystalline components connected with common atoms or atomic clusters at the interface. When composite temperature increases, the interfacial energy decreases but the system retains mechanical properties up to melting points (eutectic temperatures). The interfacial area depends on the ratio of crystalline lattice parameters of the components.

This interfacial structure will be observed at any composition in eutectic systems. The interfacial energy chosen from extremum condition of the thermodynamic function minimizes the system energy only at eutectic composition.

The proposed method can be used to calculate the interfacial energy for any composites provided that the components are insoluble in each other.

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