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EFFECTIVE VACANCY FORMATION ENERGY AND THE SOLUTE – VACANCY BINDING ENERGY IN BINARY Cu – BASED ALLOYS

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The vacancy model of melting of metals has been used as a starting point for deriving an expression permitting to determine the vacancy–impurity binding energy, E^b_{v-i}, and the effective vacancy formation energy, E^e_v, from the knowledge of the solidus line for binary alloys. The calculated values of E^b_{v-i} and E^e_v for binary Cu based alloys show a fair agreement with the experimental data existing in the literature.

Key words: vacancy – impurity interaction, phase diagrams, melting.

The vacancy-solute interaction plays an important role in the thermal diffusion and in all the diffusion-controlled processes in alloys. The interaction of solute atoms with vacancies is also of paramount importance in the production, migration and agglomeration of radiation-induced defects and especially in the growth of voids and dislocation loops. Therefore, the investigations which can bring information about this interaction are of substantial interest from both the scientific and technological viewpoints. However, the way point defects in metals interact with each other remains to be unclear. The two last reviews by March [1] and Doyama [2] show how meagre our knowledge is in this domain; the theory from first principles presents enormous difficulties, the experiments and their interpretation are also uneasy. To date the experimentally determined vacancy-solute binding energies are available essentially only for some solutes in Al, Cu and Ag [3], and only part of them can be considered as reliable.

The purpose of the present note is to draw attention to the possibility to calculate the parameters determining the concentration of vacancies in alloys from the knowledge of the solidus temperature. The basis for such calculations is the vacancy model of melting [4–6], according to which melting starts when the vacancy concentration in the solid material reaches some critical value, the same for all the metallic materials. The

comparison of the results of these calculation with the existing experimental data might be also an important test of the correctness of the proposed model of the melting process.

The thermodynamics of vacancies in dilute binary alloys has been developed by Lomer [7] and by Schapink [8]. According to Lomer, the vacancy concentration, E_v^a, at any temperature, T in an alloy of solute fraction a is given by the formula

$$C_v^a = C_v^0\left[1 - Z\cdot a + Z\cdot a\, exp\left(E_{v-i}^b/kT\right)\right], \tag{1}$$

whereas from Schapink's model it follows that

$$C_v^a = C_v^0\left[1 + a\left\{exp\left(E_{v-i}^b/kT\right) - 1\right\}\right]^Z \tag{2}$$

here E_{v-i}^b is the vacancy-solute binding energy, Z is the coordination number and C_v^0 denotes the vacancy concentration in pure solvent at temperature *T*, which can be expressed by the formula:

$$C_v^0 = A\, exp\left(-E_v/kT\right) \tag{3}$$

where A is a constant entropy factor and E_v denotes the vacancy formation energy in pure metal. Eqs. (1) and (2) hold for very dilute ($a \le 0{,}01$) alloys under assumption that the vacancy-impurity binding entropy, $S_{v-i}^b = 0$.

For more concentrated alloys both the Lomer's and Schapink's models are invalid. The equilibrium concentration of vacancies in these alloys, by analogy to the expression for a pure metal, can be written as

$$C_v^a = A\, exp\left(-E_v^e/kT\right), \tag{4}$$

where E_v^e denotes the effective vacancy formation energy in an alloy of solute fraction *a*.

According to the vacancy model of melting, the vacancy concentration in a solid alloy of solute fraction at the solidus temperature T_s should be the same as in a pure metal at the melting temperature, T_m:

$$C_{vT_m}^0 = C_{vT_S}^a \tag{5}$$

By combining Eqs. (3) and Eqs. (2) or (1) and taking into account that $E_v/T_m = 1195$ eV/K [4], one obtains, after simple transformations, the following expressions for E_{v-i}^b:

$$E_{v-i}^b = kT_s\, ln\left[\frac{exp\left[\left(T_m - T_s\right)/1195\, kT_s\right] - 1 + Z\cdot a}{Z\cdot a}\right] \tag{6}$$

from Lomer's model, and

$$E_{v-i}^b = kT_s\, ln\left[\frac{exp\left[\left(T_m - T_s\right)/1195\, kT_s\right]^{1/Z} - 1}{a}\right] \tag{7}$$

from Schapink's model. Both the models neglect the possibility of formation of solute pairs, divacancies and complicated solute-vacancy clusters, therefore the values of the vacancy-impurity binding energies calculated from Eqs. (6) and (7) depend on the solute concentration. The lower is the solute concentration, the smaller is the probability of formation of the solute-vacancy clusters and therefore it can be expected that one can obtain the true value of the solute-vacancy binding energy by extrapolating the

$E^b_{v-i} = f(a)$ dependence to the zero concentration of the alloying element. The value of E^b_{v-i} obtained in this way from the Lomer's and Schapink's models are the same [9–10].

The parameters describing formation of vacancies in some binary alloys have been recently determined from various quenching and equilibrium experiments including the Mössbauer and positron annihilation techniques. This provides the possibility to check the validity of relationships [6] and [9] as well as of the whole vacancy model of melting.

As expected, the values of the vacancy-impurity binding energy E^b_{v-i}, calculated from Eqs. (6) and (7) using the solidus temperatures taken from the available phase diagrams [11-13] differ among themselves and depend on the solute concentration. However, when extrapolated to the zero concentration of the alloying element, the dependences $E^b_{v-i} = f(a)$ calculated using the Lomer's and Schapink's models give the same value of E^b_{v-i} [9,10]. It can be assumed that such an extrapolation gives the true value of the vacancy-impurity binding energy. This supposition has been already positively verified on the example of Al – based [9] and Ni – based [10] alloys.

In table 1 the available in literature [14–22] data on the effective vacancy formation energy E^e_v for 42 binary copper alloys are collected and compared with those calculated from equation (4) using the data on the solidus temperature taken from phase diagrams published in [11–13]. The calculated values of E^e_v show a satisfactory agreement with experiment. Taking into account the possible inaccuracy of evaluation of the solidus temperatures from published phase diagrams it is fair to conclude that the average – and mean square root difference between the calculated and experimental values of E^e_v, being equal to 0,09 and 0,02 eV, respectively, are comparable with typical uncertainty of experimental determination of E^e_v (~0,02 eV). This agreement corroborates the correctness of the proposed vacancy model of melting of metallic materials.

For some alloys, however, the difference between the calculated and experimental values of E^e_v is even greater than 0,10 eV. For example, in the case of copper-germanium alloys the calculated experimental data determined using the positron annihilation techniques [19] agree with those calculated from equation (4) much better than those determined by microcalorimetric methods [20]. It seems, that the differences between the results of microcalorimetric [20] and positron annihilation investigations result from underestimation of anharmonic effects in [20], what in turn results in the underestimation of the vacancy formation energy.

Table 2 represents a comparison of the calculated values of the impurity-vacancy binding energy for various solutes in diluted Cu – base alloys, with the experimental data available in the literature. In contrast to the results obtained previously for the Al – base alloys [9], the agreement is not as good as that in Table 1. It must be noted, however that the experimental investigations of the solute-vacancy interaction in the Cu – based alloys were not so intensive as in the case of Al – based alloys.

Table 1

Calculated and experimental values of the effective vacancy formation energy E_v^e for binary Cu – based alloys

Admixture and its content in % at.		E_v^e [eV]		Admixture and its content in % at.		E_v^e [eV]	
		calc.	exp.			calc.	exp.
Ag	2,0	1,08	0,98 [14]	Ge	1,0	1,12	1,13 [19]
	2,3	1,06	0,97 [14]		2,0	1,10	1,09 [19]
Au	25,0	0,97	0,94 [15]		3,0	1,07	0,90 [20]
Al	2,0	1,13	1,17 [16]		3,1	1,07	1,07 [20]
	4,6	1,12	1,10 [14]		4,9	1,04	0,98 [18]
	8,3	1,12	1,02 [17]		5,0	1,04	0,93 [20]
	8,5	1,10	1,06 [16]		6,8	1,01	1,01 [19]
	13,7	1,04	1,00 [16]		8,0	0,99	0,75 [19]
	14,0	1,04	1,03 [16]		9,0	0,97	0,90 [20]
	15,0	1,02	1,00 [17]		9,2	0,97	0,94 [18]
	16,6	1,01	0,93 [16]		10,5	0,95	0,73 [18]
	18,0	1,01	1,00 [17]	Ni	20,0	1,17	1,25 [21]
Be	1,0	1,12	1,00 [18]		30,0	1,20	1,35 [21]
	1,5	1,11	0,93 [18]		40,0	1,23	1,43 [21]
	2,0	1,10	0,92 [18]		60,0	1,30	1,53 [21]
Ga	4,6	1,10	1,10 [17]		80,0	1,38	1,62 [21]
	8,3	1,07	1,02 [17]	Zn	5,0	1,11	1,12 [22]
	15,0	1,01	0,88 [17]		10,0	1,09	1,04 [22]
Mn	8,0	1,06	1,19 [14]		15,0	1,07	1,04 [22]
	15,0	1,01	0,99 [14]		20,0	1,05	0,99 [22]
	21,0	1,00	1,01 [14]		25,0	1,03	0,96 [22]
	25,0	0,98	1,06 [14]		30,0	1,01	1,00 [22]

Table 2

Calculated and experimental values of the effective vacancy – solute binding energy, E_{v-i}^b in binary Cu – based alloys

Solute		Al	As	Be	Ga	Ge	In	Ni	Sc	Sb	Si	Sn	Zn
E_{v-i}^b [eV]	calc.	0,09	0,16	0,10	0,06	0,11	0,14	-0,08	0,32	0,25	0,18	0,21	0,18
	exp.	0,15 [23]	0,32 [24]	0,20 [18]	0,14 [26]	0,18 [26]	0,23 [26]	-0,07 [24]	0,34 [27]	0,30 [25]	0,19 [26]	0/23 [26]	0,18 [28]

There are some evidences in the literature that the trace amount of rare earth metals (REM) may significantly affect the vacancy kinetics in host metals. Among others, the small admixture of Sc and Y suppress the spallation of oxide layers, as well as precipitation in quenched alloys upon their annealing. The most probable reason for this may be the strong interaction between the vacancies and rare earth atoms. Gupta [27] estimated that the Sc – vacancy binding energy in copper amounts 0,36 eV, in excellent agreement with the value of 0,38 eV, resulting from our calculations.

The large values of the REM – vacancy binding energies implicate that it is possible to suppress the vacancy precipitation phenomena at elevated temperatures by introducing small amounts of REM admixtures. This could improve the failure characteristics of metallic materials. Another important application of admixtures strongly attracting the vacancies may be the reduction of irradiation – induced void swelling in metals.

The results of the present investigations, together with the previous calculations of the vacancy-impurity binding energy in dilute aluminum [9] and nickel [10] alloys, strongly corroborate the vacancy model of melting of metallic materials and demonstrate its usefulness. Further studies are in progress.

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ЕФЕКТИВНА ЕНЕРГІЯ ФОРМУВАННЯ ВАКАНСІЙ ТА ЕНЕРГІЯ ЗВ'ЯЗКУ РОЗЧИН–ВАКАНСІЯ В БІНАРНИХ СПЛАВАХ НА ОСНОВІ МІДІ

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Використано вакансійну модель плавлення металів для отримання виразу, що дає змогу визначити енергію зв'язку вакансія–домішка, ефективну енергію формування вакансій з кривої солідусу подвійних сплавів. Отримано узгодження між розрахованими значеннями енергій для бінарних сплавів на основі міді та завдяки експериментальним даним.

Ключові слова: взаємодія вакансія–домішка, фазова діаграма, плавлення.

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