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# Diffusivity of carbon in copper- and silver-based composites

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Interstitial solid solutions could be formed at the matrix–fibre interface in the processing of metal matrix composites. Typically these solutions are of small concentrations and the solubility is usually diffusion-controled. To calculate the diffusivity, a model of the interstitial solid solution is used which gives the possibility of choosing whether octahedral or tetrahedral interstitial positions are occupied by the fibre atoms dissolved in the matrix. Analysis of Ag–C and Cu–C solid solutions allow a comparison of the occupation of the interstitial positions and its temperature dependences. The results obtained on the basis of non-empirical calculations predict the preferable occupation of octahedral positions up to $T \sim 1200$ K. This confirms the structure of the interstitial solid solution. In the framework of this model we calculate the heights of diffusion barriers and the temperature dependences of carbon diffusion in silver and copper hosts. © *1999 Kluwer Academic Publishers*

## 1. Introduction

The stability of the silver- and copper-matrix MMC with carbon (Ag/C and Cu/C) has been investigated previously [1–3]. By adding graphite fibres it is possible to obtain improved friction properties because of the lubricating properties of carbon. Silver-based composites are one of the most acceptable materials used for low-voltage circuit breakers. They exibit low arc erosion and low contact resistance [4]. The system Cu/C shows good thermal, electrical and mechanical properties in comparison with other copper-based MMC (see [5]). The character of the physico-chemical bonding in the reaction zone of Cu/C and Ag/C interfaces has not yet been investigated. Gnesin and Naidich [2] studied the wetting between liquid copper and SiC, and found that in alloys there was an interaction zone CuSi + C. Small amounts of silicon dispersed in the matrix suppress the interaction of copper with SiC. Carbon is insoluble in copper up to very high temperatures; its solubility does not exceed 0.02 at %. Thus a problem can arise with the wettability of carbon fibres by copper. This wettability is extraordinaruy small [6] and does not allow the composite material to be fabricated. Thus the interfacial bonding in copper–carbon composites is extremely weak [7]. Increasing interfacial strength for Cu–C is generally achieved in two ways: forcing a fibre reaction with the matrix, and making the matrix dissolve the carbon fibre. Sun and Zhang [7] studied the increase of interfacial strength by adding iron and nickel to copper. They showed that, in the case of iron doping, the $Fe_3C$ carbides are formed at the interface, realizing the chemical reaction bonding. Nickel, on the contrary, does not lead to the desirable effect and only dissolves small amounts of carbon fibres (dissolution bonding). The influence of the oxidation of copper-coated carbon fibres on the thermal stability of the coating was discussed elsewhere [8]. The formation of very dilute Cu–C interstitial alloys at the interface may be diffusion-controlled. Suery *et al.* [3] used carbon fibres and nickel-coated carbon fibres for the formation of silver-based composites. The main problem with the development of these metal–matrix composites is the poor wetting characteristic of the fibres by liquid silver (see [9]). Sometimes, the reactivity of carbon with many metals may be a barrier for composite fabrication. In the case of silver, reaction does not occur, so the technique may be employed only to improve wetting properties. To predict the diffusion behaviour of carbon it is necessary to study structure and interatomic interactions in such alloys.

In order to write the expression for the energy of the interstitial atom in different positions, it is possible to use the pertubation series on potentials in reciprocal space (PSP RS method). It is evident that this approximation will only roughly describe the basic particularities of the electronic spectrum of the solutions. This is especially true for the solutions where transition metals are chosen as alloying elements. However, as thermodynamic values are always obtained as a result of averaging over the spectrum, they are less sensitive to its particularities than, for example, optical characteristics [10]. That is why we believe that the PSP RS method can be applied to material science problems, such as the determination of the tendencies in the variation of the alloy thermodynamic functions in alloying, or to other problems determining the quantities, which are not too sensitive to details of the electron energy spectrum of metals and alloys.

Making use of the PSP RS method, we calculated the potentials of Ag–Ag, Cu–Cu, Ag–C, Cu–C, and C–C interactions in Ag–C and Cu–C alloys. The use of these potentials is two-fold. A study of occupations of tetrahedral and octahedral interatomic positions by carbon atoms was carried out on the basis of statistical thermodynamics with the obtained potentials. By exploring this result and the same interatomic potentials, the height of the diffusion barriers for a carbon atom which passes between the nearest interstitial positions and predict the diffusivity of carbon in silver and copper matrices, can be calculated.

As a final step we studied the changes in the diffusion of carbon atoms in a copper matrix with different alloying elements. The tendency to decrease the diffusivity of carbon in the presence of an additive may promote the formation of carbides at the interface, thus favouring adhesion. On the contrary, increasing the diffusivity of carbon in the matrix with dopants prevents the formation of carbide and does not lead to the desired effect. We assumed that carbon atoms in host matrices form a dilute interstitial solid solution, where carbon occupies the interstices.

The idea of "averaged" or "effective" interaction was used for the investigation of the influence of the third element upon the diffusion process in interstitial alloys. Assuming that we have a disordered substitutional alloy A–B and interstitial atoms C occupy the interstitial positions, in the case of the f c c lattice under investigation, there are one octahedral and two tetrahedral interstitial sites per atom. Only positions for interstitial atoms are considered. These positions also form the f c c lattices. All interstitial atoms are situated in the mean-field lattice potential. This potential is formed by the silver or copper and B atoms distributed on the f c c lattice sites. The diffusivity of carbon atoms in pure silver and copper matrices and in a copper matrix with additives, is compared.

## 2. Occupation of interstitial positions

Let us assume that interstitial atoms of carbon, C, occupy both octahedral and tetrahedral positions in the lattice. The number of octahedral positions is $M_o$ and the number of tetrahedral positions is $M_t$. Thus, the total number of intestitial positions is $M = M_o + M_t$. The $n$ atoms of carbon are placed in the interstial positions in the following manner: $n_o$ atoms in octahedral positions and $n_t$ atoms ($n_t = n - n_o$) in tetrahedral positions. That part of the total energy of the crystal depending on the number of interstitial atoms may be written as

$$E = n_o u_o + n_t u_t \tag{1}$$

assuming that carbon atoms do not interact with each other. This assumption is reasonable because the concentration of carbon is very small. Here $u_o$ and $u_t$ are the energies of carbon atoms in the octahedral and tetrahedral positions, respectively. The number of different permutations of carbon atoms on the interstitial positions is

$$L = \frac{M_o!}{n_o!(M_o - n_o)!}\frac{M_t!}{n_t!(M_t - n_t)!} \tag{2}$$

while the entropy of the system, $S$, is

$$S = k \ln L \tag{3}$$

where $k$ is the Boltzmann constant. Substituting $n_t = n - n_o$ and making use of the Stirling formula, we obtain the free energy $F = E - TS$ in the form

$$\begin{aligned} F = n_o u_o + (n - n_o)u_t - kT\{&\ln M_o! - n_o(\ln n_o - 1) \\ &- (M_o - n_o)[\ln(M_o - n_o) - 1] \\ &+ \ln M_t! - (n - n_o)[\ln(n - n_o) - 1] \\ &- (M_t - n + n_o)[\ln(M_t - n + n_o) - 1]\} \end{aligned} \tag{4}$$

Applying the equilibrium conditions $\partial F/\partial n_o = 0$, the following equation for the equilibrium numbers $n_o$ and $n_t$ may be obtained

$$\frac{(M_t - n_t)(n - n_t)}{(M_t - n + n_o)n_o} = \frac{(M_o - n_o)n_t}{(M_t - n_t)n_o} = \exp\left(\frac{u_o - u_t}{kT}\right) \tag{5}$$

It is easy to see that when the temperature increases, the system of carbon atoms seeks a uniform distribution of carbon atoms on the interstitial positions. In this case (at $T \to \infty$) we obtain $(n_t/n_o) = (M_t/M_o)$.

To clarify the temperature dependence of $n_o$ and $n_t$, Equation 5 may be solved giving

$$n_o = \frac{M_o + n - M_t\mu - n\mu \pm [(M_o + n + M_t\mu - n\mu)^2 - 4M_o n(1 - \mu)]^{1/2}}{2(1 - \mu)} \tag{6}$$

Here we use the equality $n_t = n - n_o$ and notified $\mu = \exp[(u_o - u_t)/kT]$. Using the definition of partial concentrations of atoms in octahedral and tetrahedral interstial positions $c_o = n_o/n$ and $c_t = n_t/n$, respectively, the following result may be obtained

$$\begin{aligned} c_o &= \frac{\alpha + \beta \pm [(\alpha+\beta)^2 - 4\beta]^{1/2}}{2\beta} \\ c_t &= 1 - c_o \end{aligned} \tag{7}$$

where $\alpha = 1 + (M_t/M_o)\mu$; $\beta = \gamma(1-\mu)$; and $\gamma = n/M_o$. For relatively small $n$, this result has to transform to the Boltzmann distribution. This condition leads to the consideration that only the minus sign before $[(\alpha + \beta)^2 - 4\beta]^{1/2}$ in Equation 7 has to be left and in this case from Equation 5 it follows that

$$c_o = \left(1 + \frac{M_t}{M_o}\mu\right)^{-1} \tag{8a}$$

$$c_t = \left[1 + \left(\frac{M_t}{M_o}\mu\right)^{-1}\right]^{-1} \tag{8b}$$

When the value $\gamma$ is small, the value of $\beta$ is also small and the square root may be expanded in Taylor's series. Then from Equation 7 in the limiting case $\gamma \to 0$ we get $c_o = 1/\alpha$ which coincides with Equations 8a and b.

In the case of the fcc lattice with $N$ lattice sites, $M_o = N$ and $M_t = 2N$. Thus, the final expressions for the concentrations $c_o$ and $c_t$ have the forms

$$\begin{aligned} c_o &= \left[1 + 2\exp\left(\frac{u_o - u_t}{kT}\right)\right]^{-1} \\ c_t &= \left[1 + \frac{1}{2}\exp\left(\frac{u_t - u_o}{kT}\right)\right]^{-1} \end{aligned} \tag{9}$$

## 3. Diffusion of interstitial atoms

The basic idea of effective interaction may become of use for the investigation of the influence of the third element upon the diffusion process in interstitial alloys. We assume that atoms B substitute for atoms A, and atoms C are placed in the interstitial position. The value of the energy of atom C in the interstice position, $u_o$, is

$$\begin{aligned} u_i = -\sum_{\boldsymbol{R}} \{ & V_{AC}(\boldsymbol{R} + \boldsymbol{h}_i) C(\boldsymbol{R}) \\ & + V_{BC}(\boldsymbol{R} + \boldsymbol{h}_i)[1 - C(\boldsymbol{R})]\} \end{aligned} \tag{10}$$

where $\boldsymbol{h}_i$ is the vector of the position of the atom C. $V_{AC}$ and $V_{BC}$ are the values of the interaction potentials between atoms A and C, and B and C, respectively. $C(\boldsymbol{R})$ is the spin-like variable

$$C(\boldsymbol{R}) = \begin{cases} 1, & \text{if an atom in the lattice site } \boldsymbol{R} \text{ is of the type A} \\ 0, & \text{if an atom in the lattice site } \boldsymbol{R} \text{ is of the type B} \end{cases}$$

Consequently, the energy of the C atom in the saddle point $u_s$ is

$$\begin{aligned} u_s = -\sum_{\boldsymbol{R}} \{ & V_{AC}(\boldsymbol{R} + \boldsymbol{h}_s) C(\boldsymbol{R}) \\ & + V_{BC}(\boldsymbol{R} + \boldsymbol{h}_s)[1 - C(\boldsymbol{R})]\} \end{aligned} \tag{11}$$

$\boldsymbol{h}_s$ is the vector of the saddle point position. Equations 10 and 11 reproduce exactly the local atomic configuration in the vicinity of the interstitial atom in the diffusion process. Consideration of such local effects is very important in the study of material properties (see, for example, [11]). Calculations of $\bar{u}_i$ and $\bar{u}_s$ may provide the necessary information on the influence of microalloying additives on the diffusion coefficient. On performing these calculations in the framework of the cluster approach, one obtains the local values of $\bar{u}_i$ and $\bar{u}_s$. These quantities have to be averaged to account for the influence of a crystal medium [12].

The alternative way is to introduce the distribution of atoms in A–B substitutional solid solution. This distribution may be described by one occupation probability function $n(\boldsymbol{R})$ that is the probability of finding the atom A at the site $\boldsymbol{R}$ of the crystal lattice

$$n(\boldsymbol{R}) = \langle C(\boldsymbol{R}) \rangle \tag{12}$$

where the averaging is done over the Gibbs' canonical ensemble. Performing such averaging we may rewrite Equations 10 and 11

$$\begin{aligned} \bar{u}_i = -\sum_{\boldsymbol{R}} \{ & V_{AC}(\boldsymbol{R} + \boldsymbol{h}_i) n(\boldsymbol{R}) \\ & + V_{BC}(\boldsymbol{R} + \boldsymbol{h}_i)[1 - n(\boldsymbol{R})]\} \end{aligned} \tag{13}$$

$$\begin{aligned} \bar{u}_s = -\sum_{\boldsymbol{R}} \{ & V_{AC}(\boldsymbol{R} + \boldsymbol{h}_s) n(\boldsymbol{R}) \\ & + V_{BC}(\boldsymbol{R} + \boldsymbol{h}_s)[1 - n(\boldsymbol{R})]\} \end{aligned} \tag{14}$$

Analogous averaging was done by Khachaturyan [13] to describe the ordering effects in a binary substitutional solid solution. Let us consider the case where all positions of crystal lattice sites $\{\boldsymbol{R}\}$ are described by one Bravais lattice. Following the works of Khachaturyan (see [13] and references therein), the function $n(\boldsymbol{R})$, which determines the distribution of the solute atoms in an ordering phase, can be expanded in a Fourier series. It may be represented as a superposition of static concentration waves (SCW)

$$n(\boldsymbol{R}) = c_a + \frac{1}{2}\sum_j [Q(\boldsymbol{k}_j)\, e^{i\boldsymbol{k}_j \boldsymbol{R}} + Q^*(\boldsymbol{k}_j)\, e^{-i\boldsymbol{k}_j \boldsymbol{R}}] \tag{15}$$

where $c_a$ is a concentration of A-type atoms, $exp(i\boldsymbol{k}_j \boldsymbol{R})$ is a static concentration wave, $\boldsymbol{k}_j$ is a non-zero wave vector defined in the first Brillouin zone of the disordered binary A–B alloy, index $j$ denotes the wave vectors in the Brillouin zone, $Q(\boldsymbol{k}_j)$ is a static concentration wave amplitude. As shown by Khachaturyan [13], all $\boldsymbol{Q}(\boldsymbol{k}_j)$ are the linear functions of the long-range order parameters of the superlattices that may be formed on the basis of the Ising lattice of the disordered solid solution. In the alloy with a small concentration of one of the components it is possible to assume the existence of a disordered solid solution. The small concentration of the B atoms immediately leads to the disappearance of the ordering state and all $Q(\boldsymbol{k}_j)$ become equal to zero.

We consider now a disordered substitutional alloy A–B with interstitial atoms C. In the case of the f c c lattice studied here, there are one octahedral and two tetrahedral interstitial sites per atom. We shall consider only the octahedral positions for interstitial atoms. This model follows from the results of the calculations for occupation probabilities for Cu–C which will be discussed in the next section. These octahedral positions are also forming the f c c lattice and, in the case of completely disordered solid solution, they are energetically equivalent. All interstitial atoms are situated in the same mean-field lattice potential. This potential is formed by the A and B types of atoms randomly distributed on the f c c lattice sites. Making use of the above described averaging, it is possible to calculate the influence of alloying elements upon the diffusion of fibre atoms (named C) in the matrix (atoms A). The concentrations of atoms of sort A and B will be $c_a$ and $c_b$, respectively. Taking into account only the first and second nearest neighbours, we have from Equations 13 and 14

$$\begin{aligned}\bar{u}_i &= -\left[6(c_a v_{ac} + c_b v_{bc}) + 8\left(c_a v'''_{ac} + c_b v'''_{bc}\right)\right]\\ \bar{u}_s &= -\left[2\left(c_a v'_{ac} + c_b v'_{bc}\right) + 4\left(c_a v''_{ac} + c_b v''_{bc}\right)\right]\end{aligned} \tag{16}$$

where $v_{ac} = V_{ac}(a/2)$, $v'_{ac} = V_{ac}(a\sqrt{2}/4)$, $v''_{ac} = V_{ac}(a\sqrt{6}/4)$, $v'''_{ac} = V_{ac}(a\sqrt{3}/2)$, $v_{bc} = V_{bc}(a/2)$, $v'_{bc} = V_{bc}(a\sqrt{2}/4)$, $v''_{bc} = V_{bc}(a\sqrt{6}/4)$, $v'''_{bc} = V_{bc}(a\sqrt{3}/2)$ are the values of the interatomic interaction energies determined from the values of interatomic interaction potentials $V_{ac}$ and $V_{bc}$ between atoms of sort A and C, and B and C, respectively. $a$ is the lattice parameter of the alloy. We used in our calculations the model potential from Bachelet *et al.* [14]. The height of potential barrier is

$$\begin{aligned}\Delta U = |\bar{u}_s - \bar{u}_i| = \big|&\left(6v_{ac} + 8v'''_{ac} - 2v'_{ac} - 4v''_{ac}\right)c_a\\ &+ \left(6v_{bc} + 8v'''_{bc} - 2v_{bc} - 4v''_{bc}\right)c_b\big|\end{aligned} \tag{17}$$

The values in brackets here have the sense of the heights of barriers $\Delta U_a$ and $\Delta U_b$ in the diffusion process of C atoms in the metals A and B with an f c c lattice. The diffusion coefficient of C atoms that are situated in the octahedral interstices of disordered substitutional solid solution A–B with an f c c lattice, may be obtained by substituting this expression into Arrhenius-type formulae

$$D \sim exp\left(-\frac{\Delta U}{kT}\right) \tag{18}$$

giving

$$D \sim exp\left(-\frac{c_a \Delta U_a + c_b \Delta U_b}{kT}\right) \tag{19}$$

It is easy to see that the activation energy in our approximation is a linear function of concentration $c_a$. Let us turn now to the study of the changes of pre-exponential factors caused by alloying. The Gibbs' free energy of migration includes the entropy term and the pressure-dependent term. The last can be neglected because we are studying the diffusion process at the atmospheric pressure that in our units is approximately zero. The entropy of migration in a binary alloy A–C may be calculated, according to Shewmon [15], with our values for the migration energy, $\Delta U$

$$S_{mig} = \beta \frac{\Delta U}{T_m} \tag{20}$$

where $\beta \simeq 0.35$ [15] and $T_m$ is the melting point. Now we may write the following relation

$$\frac{D_{tern}}{D_{bin}} \simeq \frac{a^2_{tern}}{a^2_{bin}} exp\left[\frac{(1-\beta\tau)}{kT}\left(\Delta U^{bin}_{mig} - \Delta U^{tern}_{mig}\right)\right] \tag{21}$$

where $D_{tern}$ and $D_{bin}$ are the diffusion coefficients of the carbon in ternary and binary alloys, respectively, $\tau = T/T_m$ and $\Delta U^{tern}_{mig}$ and $\Delta U^{bin}_{mig}$ are the migration energy for ternary and binary alloys.

Our model is of the common nature and could be used for the calculations of diffusivity in the pure host assuming the atomic fraction of the dopant (C-atoms) is equal to zero.

## 4. Results and discussion

Our mean-field calculations in the framework of local density approximation with semiempirical potentials show the completely different character of C–C interaction in the matrix of diamond and in the copper matrix. The same character of C–C interactions is present in the silver host. In both matrices, the C–C pair potential has a very strong repulsive tendency and in the diamond lattice the behaviour of the pair potential is traditional.

The interatomic potential presented in Fig. 1 was used to calculate the carbon atom energies in different interstitial positions $u_o$ and $u_t$ in the copper and silver matrix. In these calculations we take into account the interaction in the first and the second coordination shell. The energies $u_o$ and $u_t$ were substituted in Equation 9 and the temperature dependence of the relative concentrations $c_o$ and $c_t$ were obtained. They are

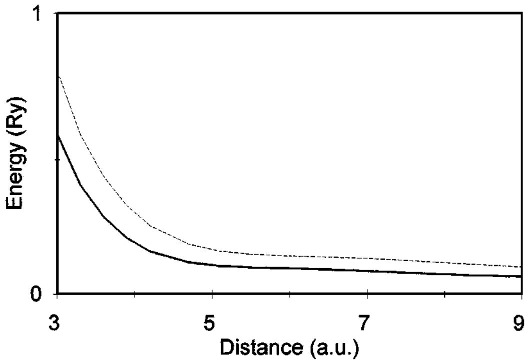

*Figure 1* The effective pair potentials (——) of Cu–C, and (- - -) Ag–C in Ag- and Cu-based metal matrix composite.

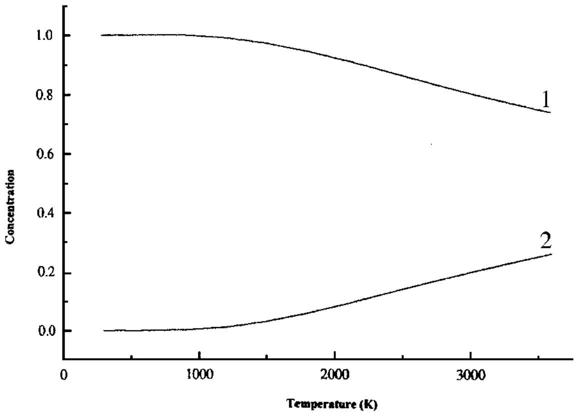

*Figure 2* Temperature dependences of partial concentrations of carbon atoms occupying (1) octahedral and (2) tetrahedral interstitial positions in a copper matrix.

plotted in Fig. 2 for the copper host matrix. An analogous behaviour is obtained for Ag–C.

Our results show clearly that the probability of finding carbon atoms in octahedral positions is much higher than in tetrahedral ones. This statement will be true up to a temperature $T \sim T_o = 1200\,K$. With the following increase in the temperature, the occupation probability of octahedral positions decreases to 80% for copper based alloy. Tetrahedral positions will be occupied by 20% of the atoms. Thus we are convinced that the model of the interstitial diffusion of carbon atoms can be used in solid solutions with the carbon atoms randomly situated in octahedral positions. This model is justified at least up to $T \sim T_o$. Equations 16 and 17 are used to calculate diffusion barriers. We calculated interatomic potentials for the ternary alloys (Cu, Ti)–C, (Cu, Al)–C, and (Cu, Ni)–C making use of mean-field theory and form-factors of semiempirical potentials from Bachelet *et al.* [14]. The concentration of carbon atoms in an alloy was taken to be very small ($\sim 2 \times 10^{-2}$ at %), and the concentration of elements that alloy the copper matrix was taken as 0.1 at %. The values of potential barrier, $\Delta U$, for binary alloys Ag–C and Cu–C are given in the Table I. We may conclude from analysis of Table I that alloying of the binary system Cu–C by all studied additives, increases the height of the potential barrier.

Let us turn now to the study of the changes of pre-exponential factors caused by alloying. The Gibbs' free energy of migration includes the entropy term and the pressure-dependent term. The last can be neglected because we are studying the diffusion process at the atmospheric pressure which in our units is approximately zero. The entropy of migration in a binary alloy A–C may be calculated, according to Equation 20, with the obtained values for the migration energy $\Delta U$. The values of migration entropies, $S_{mig}$, are also presented in Table I.

TABLE I Values of diffusion barriers, $\Delta U$, entropies of migration, $S_{mig}$, and the ratio $D_{tern}/D_{bin}$ for the interstitial silver- and copper-based alloys with carbon

| Host | Dopant | $S_{mig}$ ($10^4$ eV K$^{-1}$) | $\Delta U$ (eV) | $D_{tern}/D_{bin}$ |
|---|---|---|---|---|
| Ag | None | 8.898 | 3.16 | – |
| Cu | None | 2.554 | 0.990 | – |
| Cu | Al | 2.603 | 1.009 | 0.805 |
| Cu | Ni | 2.575 | 0.998 | 0.912 |
| Cu | Ti | 2.652 | 1.028 | 0.647 |

In order to estimate the changes in the diffusion coefficient we have calculated the ratio $D_{tern}/D_{bin}$. In these calculations we used Vegard's law for the changes of the lattice parameters in dilute alloys. We have also assumed that the effective frequency of the atomic vibrations for studied alloys is independent of the alloying. The ratio of lattice constants, $a^2_{tern}/a^2_{bin}$, for the (Cu, Ti)–C alloy only slightly deviates from unity and is equal to 1.000 65. Thus it is possible to neglect this effect in studying the changes of diffusion coefficient at small concentrations. Using the data of Table I, we estimated the ratio $D_{tern}/D_{bin} = 0.647$ for (Cu, Ti)–C alloy at 800 K. The same calculations were performed for copper-carbon alloy with a set of dopants (see Table I). All investigated additives decrease the diffusivity of carbon atoms in a copper matrix. On the basis of the data in Table I, we predict that the strongest influence on the diffusion coeficient ratio among the investigated additives may be achieved by titanium alloying of the Cu–C system. The predicted reduction of the diffusivity by a factor of two may be a basis for detailed experimental study of routes of improvement of carbon fibre interactions with a copper-based matrix.

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