# Thermo-Mechanical Aspects of the Phenomenon of Selective Mass Transfer by Diffusion in Friction Process of Steel/Copper Alloy Couple

**Filip Ilie**
Department of Machine Elements and Tribology, Polytechnic University of Bucharest,
313 Spl. Independentei, 060042
Bucharest, Romania
E-mail: ilie.filip@yahoo.com

***Abstract*— In the process of friction of two materials and in the presence of own lubricants, the wear phenomenon itself manifests as a transfer of material from an element of a friction couple on the another, this phenomenon being characteristic of selective mass transfer process by diffusion, forming a thin, superficial layer with superior properties, at minimum friction and wear. A selective mass transfer by diffusion can be safely achieved in friction couples, steel/copper alloy lubricated with glycerin or a special lubricant, where sure takes place, a mass transfer by copper diffusion, on the friction surface of the steel, if there is a favorable energy and in the presence of the relative movement. A phenomenon that accompanying the material transfer through diffusion in the friction process, is the thermal diffusion. The paper analyses the mass transfer phenomenon through diffusion, with the thermal issues (thermal diffusion), which leading to the formation of soft, thin and superficial layer, tribological performance, and, the correlation between the thickness of this layer and the saturation degree of the contact surfaces of the couple friction from steel/copper alloy (bronze, brass).**

***Keywords—selective mass transfer; thermal diffusion; saturation degree; friction couple***

## I. INTRODUCTION

Diffusion in metallic materials has a fundamental role in the processes of extraction and purification of metals and alloys, and in processing technology [1, 2, and 3]. Mass transfer by diffusion is done by moving atoms and therefore, the diffusion in solid state allows information on thermal agitation of the atoms in the crystal lattice and of structural imperfections present in the network [4]. The knowledge of laws which rule the diffusion phenomena and mass transfer are important in the establishing of some kinetic relationships [5, 6], through the technological parameters correlation (concentration, temperature, contact duration etc.), which allow a the quantitative appreciation of transfer processes and it making possible the intervention in their modification, for intensifying the process and for establishing the optimum conditions for carrying it out [7].

The mechanism of the mass transfer by diffusion includes:

- diffusion and mass transfer of the reactants at the interphase separation limit;
- physic–chemical transformations at the interface;
- diffusion and mass transfer of the reaction products at the elements interface in contact.

At the analysis of the diffusion phenomenon and of the mass transfer are necessary to solve:

- conditions for the realization of a certain number of phases and the laws describing the components distribution, between they, determined through the laws of the phases and laws of the equilibrium;
- conditions for the phenomena development (operational conditions), determined by the initial and final conditions of the components and their quantities; the relations between the components concentrations and quantities are obtained from the mass conservation law (material balance equation );
- conditions which determine the diffusion speed and the mass transfer's speed from a surface on another and its dependence of the difference between the equilibrium concentrations and operational, of the system's physical properties and of the thermal conditions from the contact area.

It is known that in the solid materials the diffusion mechanism is a jump mechanism, the mass transfer is done through successive, activated thermal jumps of the atoms, from the old position to a neighboring atomic position, from a surface to another [7, 8]. The way how occurs the diffusion process into solids is presented, schematized in Fig. 1, where is showing the distribution of atoms, in the moment $t = t_o$, from the beginning of diffusion, when the atoms which diffuses are uniform distributed in the central part (Fig.1a), after the time $t = t_1$ relative small from the beginning of diffusion and after the time $t = t_2$ relative big from the beginning of this process, respectively how varying with the distance $z$, the concentration $c$, of the atoms alloying at the same moments (Fig.1b).

The most probable, diffusion mechanism in solid solutions is diffusion through the vacancies. Mathematic, the diffusion in metals and the solid alloys is described with the help the Fick's laws, quantitatively describing at microscopic level, the mass transport by diffusion [2, 7, and 8]. The first law describes the speed with which is produces the diffusion and is shown by the relationship:

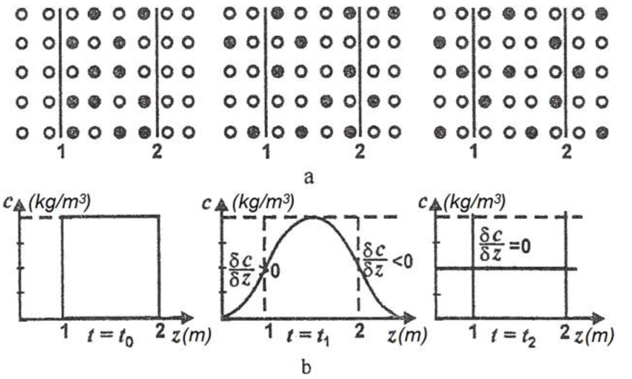

Fig. 1 *Diffusion process in the solid solutions of substitution of metal B in A (a) and the variation with distance z of concentration c of the diffusing atoms (b):*
*• - atoms of the base constituent A (Fe);*
*o - atoms of the constituent which diffuses B (Cu)*

$$J = D\,grad\,c, \tag{1}$$

or the diffusion after a direction *z*, will be:

$$J = D(\,\partial c/\,\partial z\,) \tag{2}$$

where: *J* – the material flow, which diffuses and passes through the surface unit in time unit, in (kg/m$^2$s); *D* – diffusion coefficient, in (m$^2$/s); *c* – constituents concentration, in (kg/m$^3$); *z* – direction (distance), in (m).

If the *c* is expressed in kg/m$^3$), then the *J* is denoted by *m* - mass flow, in (kg/m$^2$s) and is equal to the amount of material in (kg), passing in one second through a section equal to unity.

The modification of concentration in time is described by second Fick's law:

$$\partial c/\,\partial t = div(D\,grad\,c), \tag{3}$$

and for the diffusion after a direction, becomes:

$$\partial c/\partial t = D(\,\partial^2 c/\partial z^2). \tag{4}$$

For the execution of a diffuse atomic jump is necessary the existence of a very big fluctuation of the atoms vibration energy, correlated with an adequate synchronization of the neighbors atoms movement and is realized through the average frequency of atomic jump, expressed by the relationship:

$$J = -(1/z)(\nu_o a^2 e^{\,-E_a/RT}). \tag{5}$$

By identifying of the relationships (1) and (3) obtain:

$$D = (1/z)(\nu_o a^2 e^{-E_a/RT}) = D_o e^{-E_a/RT}, \tag{6}$$

in which: *z*- coordination number of the network; $\nu_o$ - vibration frequency of the atoms, $\nu_o$ = 10$^{13}$ s$^{-1}$; *a* – distance between two atomic equilibrium positions which are neighboring in the network, in (m); $E_a$ = activation energy, depending on how diffusion occurs [9, 10], in (J); $D_0$ - the frequency factor, dependent of the coordination number (interstitial available positions), vibration frequency of diffused particles and of the distance between interstitial surfaces.

In (4) of the diffusion coefficient, the inter-atomic distance in the network *a*, varies very little with the temperature, having close values for all metals. As a result, the diffusion coefficient *D* varies rapid with the temperature and is different in alloys, because of the jump average frequency variation, having values of 10$^{-8}$ m$^2$/s, and $D_0$ is independent of the temperature, and for metals and the solid alloys is between the 10$^{-3}$ – 10$^{-1}$ m$^2$/s limits [7, 8, and 9].

## II. THERMAL DIFFUSION AND SELECTIVE MASS TRANSFER BY DIFFUSION

The diffusion mechanism in solids, being a jump mechanism, the mass transfer (transport) is made through successive jumps from a position of equilibrium to another. Both forms of diffusion are possible: self-diffusion and inter-diffusion. In real solids, the principal mechanisms depend of the defects and the solid solution type (alloys type): diffusion through interstice and diffusion through vacant nodes.

The temperature gradient can lead to mass transfer from a surface on another when the energetic conditions from the contact area are ensured. The thermal diffusion in metals and alloys can have place only through the crystalline network, on the surface or at the grain limit. Many investigations showed that thermal diffusion develops the fastest at the element's surface, a bit slower at the grain's limit and the slowest in the grains volume [7, 8, and 10]. So, for the case considered in this paper, the thermal diffusion at selective mass transfer is a surface diffusion, after how it will see further.

Similarly, the concentration gradient *c* through thermal gradient (Dufour effect) it can transfer mass from a surface on another. The second Fick's differential equation is [9, 10]:

$$\partial c/\,\partial t = (\,\partial/\,\partial z)[D((\,\partial c/\,\partial z) + (\,\partial\alpha/\,\partial z)(c/\alpha_e))],$$

and for solids $\alpha_e = A\,e^{(\,-E_a\,/\,R\theta\,)}$, (7)

with *A* – constant; $E_a$ - activation energy, in (J); *R* – gas universal constant, in (J/mol K); $\theta$ - temperature, in (K).

Differentiating (7) after direction *z* and neglecting second order differentials, obtained:

$$\partial c/\,\partial t = \,\partial/\,\partial z[\,D(\,\partial c/\,\partial z\,)] - (1/R)\,\partial/\,\partial z(\,Dc/\theta\,)$$

$$\partial E_a/\,\partial z + (1/R)\,\partial/\,\partial z(\,DcE_a/\theta^2\,)\,\partial\theta/\,\partial z \tag{8}$$

The first part of (8) $\partial/\,\partial z(\,(D\,\partial c/\,\partial z)$, represents Fick's second law in the classic way, and the other components are effects of temperature (Dufour effect).

For solid materials, the diffusion coefficient *D* has a dependence of Arrhenius type (see (6)), where $T = \theta$.

Defining concentration flow $J = (\partial / \partial z)[D(z,t)\, c(z,t)]$ and according (6) results [11, 13, and 14]:

$$J = (Dc/R\theta)(\, \partial E_a / \partial \theta - E_a/\theta\,)\, d\theta/dz - Ddc/dz \quad (9)$$

Equation (9) shows that, if $\partial E_a / \partial \theta = E_a / \theta$, then thermal diffusion doesn't happen; if $\partial E_a / \partial \theta \leq E_a / \theta$, thermal diffusion occurs from the lowest temperature to the highest; if $\partial E_a / \partial \theta \geq E_a / \theta$, occurs from the highest temperature to the lowest, the flow *J* may be null, if the two terms are equal. Using Fick's second law is inferred differential equation of thermal diffusion [13, 15, and 16]:

$$\partial c / \partial t = \partial^2 [\, D(z,t)\, c(z,t)\,] / \partial z^2 \quad (10)$$

If materials of friction couple have different concentrations of some of the component elements and in the friction area there are energetic formed conditions and a liquid with properties which avoids the oxidation and penetration of hydrogen, then thermal diffusion is possible and, as result, (10) can be applied. For the bronze/steel couple the lubricated with glycerin, copper can diffuse from bronze, on the steel surface, forming through mass transfer a layer „servowitte". If we consider a bronze roughness 1 in contact with steel surface 2 (Fig. 2) with Oz axe orientated in steel surface, then the differential equation of the diffusion process is obtained from (11):

$$(\, \partial c / \partial t\,) = -(\, \partial J / \partial z\,)\,. \quad (11)$$

Solution of (11) is done for the next initial and at limit conditions:

$$\begin{cases} 1)\ c = 0,\ \ t = 0,\ \ z > 0; \\ 2)\ D(\, \partial c / \partial z)_{z=0} = const = m, t > 0, z = 0 \\ 3)\ c = 0,\ \ t > 0,\ \ z \rightarrow \infty \end{cases},$$

where *m* is constant mass flux on contact area, and they lead to the solution:

$$c(z,t) = m/\sqrt{D}[2\sqrt{t/\pi}\; e^{-z^2/4Dt} - z/\sqrt{D}\; erf\, c(z/2\sqrt{Dt}\,)], \quad (12)$$

To see how, the concentration *c* varies with the surface depth *z* and function time *t* in the conditions of the mass transfer, has been resolved (10) and plotted in Fig. 3, as *c/m = f (z, t)* for a known diffusion coefficient $D = 3 \cdot 10^{-14}$ m$^2$/s, where it see that the concentration, increases in time and decreases with depth from the surface depth.

To have a quantitative correlation with the experimental results, has been represented graphic, also the concentration's variation with *z* from the surface depth after an hour functioning of the friction couple (Fig. 4); and with the functioning time in conditions of diffuse mass transfer, for depth *z* = 3 μm (Fig. 5) and the same *D*, confirming results in Fig. 3.

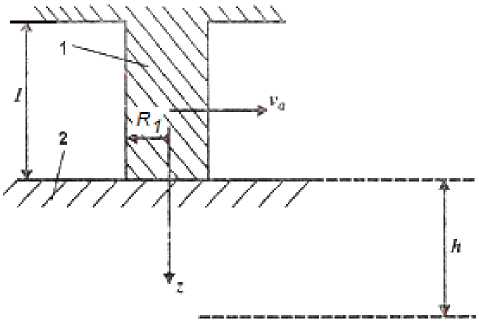

Fig. 2 Roughness from bronze in contact with a steel surface: 1-roughness; 2 –steel surface

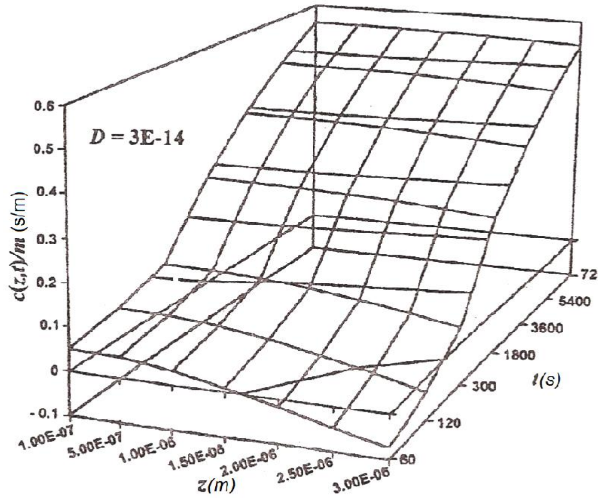

Fig. 3 Concentration's variation c (z, t) with the depth from the surface *z* and time *t* in the conditions of mass transfer by diffusion

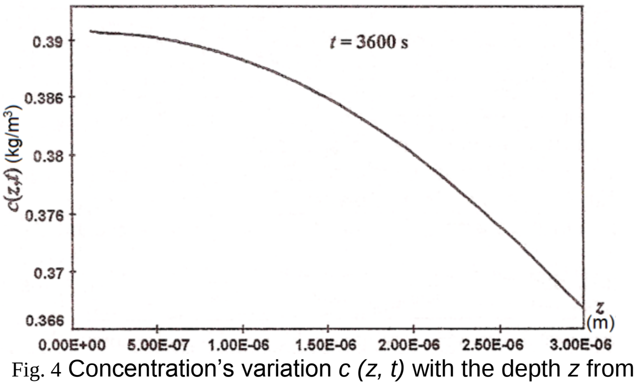

Fig. 4 Concentration's variation *c (z, t)* with the depth *z* from the surface, after *t* = 3600 s

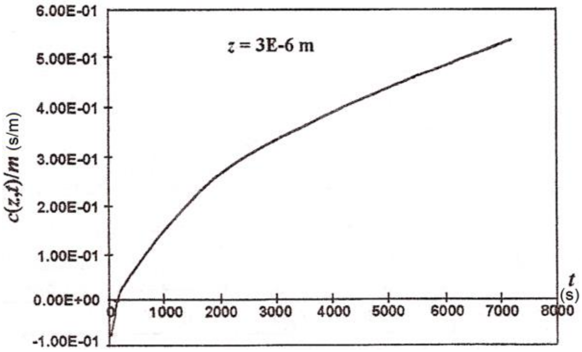

Fig. 5 Concentration's variation *c (z, t)* with the functioning time *t* at depth *z* = 3 μm

A correlation example for the above dates using (11) and the graphic representations (Fig. 3, 4, 5) have allowed the establishing of concentration copper in steel, $c$ = 367 kg/m$^3$, with whose help was possible to obtain to bronze/steel couple the mass flow, $m \approx 10^{-9}$ kg/m$^2$s, that corresponds as order of magnitude with the specialty literature values.

Solutions (12) allow and analyze the temperature's effect through parameter $D$ (which depends of temperature) on variation of copper concentration with time $t$ and with the depth from steel surface 2.

It is observed as the effect of parameter $m$ is very important for diffusion. It is noteworthy that the values of this parameter, possible by determined experimental, are dependent of the used lubricant and the local conditions of creation of the energetic transfer. The formed local area can be considered as a „membrane" of diffusion mass transfer [14]. This „membrane" can be completely the opaque and the transfer doesn't appears or absolutely permeable and the transfer is maximum. The „membrane" must have such properties, so that the diffusion the transfer to be made in both directions.

## III. CORRELATION BETWEEN TRANSFERRED LAYER'S THICKNESS AND THE SATURATION DEGREE

Defining, the transferred layer by diffusion in the mass transfer conditions as a layer of thickness $h = k\sqrt{Dt}$ , in which was transferred a certain percentage copper quantity ($k$ – constant, determined in function of the percentage of substance transferred). Considering, the quantity of accumulated substance in the layer of thickness $h$ ($M_h$) and the quantity of substance accumulated the whole body of height $l$ ($M_l$) ($l > h$) (see Fig. 2), by the transfer on the contact area $A_c$, obtain:

$$M_h = A_c\int_0^h c(z,t)dz \text{ and } M_l = A_c\int_0^1 c(z,t)dz. \tag{13}$$

Replacing in (12), $z = h = k\sqrt{Dt}$ and $u = z/2\sqrt{Dt}$, results $M_h$, from (13) ($M_h = \Phi(k/2)$), respectively $z = l$, results $M_l$, from (13) ($M_l = \Phi(k/2)$), where: $\phi(k/2) = (2/\sqrt{\pi})\int_0^{k/2} e^{-u^2}du$, solvable numerically according with Table I.

For $l \to \infty$, results $M_\infty = 2m\,A_c \cdot t$. Defining the saturation degree of the concentration $g_s = M_h/M_\infty$, results:

$$g_s = \varphi(k/2) - \frac{1-\varphi(k/2)}{4}k^2 = \frac{1}{4}[(4+k^2)\varphi(k/2) - k^2], \tag{14}$$

whose variation is given in Fig. 6.

TABLE I

| k | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $\varphi(k/2)$ | 0.5205 | 0.8427 | 0.9661 | 0.9953 | 0.9996 | 1.000 |

*Solve numerical a function* $\varphi(k/2)$

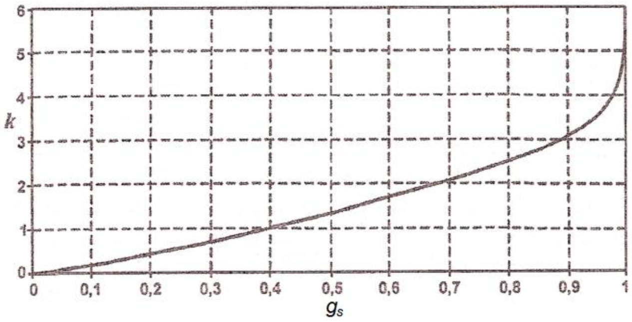

Fig. 6 The variation's saturation degree of at the copper concentration in bronze/steel surface

If it accept a certain saturation degree ($g_s$) of the steel surface with copper from bronze, then is possible to determine the constant $k$ and the quantity of substance in a layer $h = k\sqrt{Dt}$ . The relative saturation ($g_r$) of the steel couple with the copper from bronze is:

$$g_r = \frac{M_h}{M_l} = \overline{D}\frac{(4+k^2)\Phi(k/2) - k^2}{(4\overline{D}+1)\Phi(1/2\sqrt{\overline{D}}) - 1}, \tag{15}$$

and the way how varies with $D$ is presented in Fig. 7.

The dimensionless parameter $\overline{D} = Dt/l^2$, similar to Fourier parameter ($F_0$) in the thermal transfer, it can be explained depending on the geometry elements of the couple and by the relative sliding speed, rolling and pivoting speed and the their combinations. So, for a cylindrical roughness 1 (with ray $R_1$ and height $l$) with contact on flat circular frontal surface and which moves with a relative sliding speed $v_a$ (see Fig. 2), girl of ideal plane surface (without roughness), the dimensionless parameter will be:

$$\overline{D}_1 = D_1(\theta) l_f / v_a l^2, \tag{16}$$

where: $l_f$ - friction length, in (m); $D_1(\theta)$ - diffusion parameter of the roughness material at the contact surface temperature.

For the ideal plane surface of $h_1$ (m) thickness, the material having the diffusion parameter $D_2(\theta)$, the dimensionless parameter will be:

$$\overline{D}_2 = D_2(\theta) 2R_1 / v_a h_1^2. \tag{17}$$

For an un-according roughness (spherical or cylindrical with a punctual or linear contact), the contact time and of transfer through diffusion is dependent of the real contact area's size and of the relative speed.

So, the principal cause of the diffusion mass transfer is variation of the thermal conditions, both in time, and in the near of the friction surface, demonstrated by analytical calculation of the transferred layer thickness.

## IV. CONCLUSIONS

- Selective mass transfer by diffusion is done by successive, activated thermal jumps of the atoms, from one position to another, from a surface to another.
- Mass transfer by diffusion allows obtaining information on: thermal agitation of the atoms in the

crystal lattice and of structural imperfections present in the network.

- The diffusion mass transfer is described mathematically with the help the Fick's laws.
- The knowledge of laws which rule the diffusion phenomena and mass transfer are important to the technological parameters correlation (concentration, temperature, contact duration etc.).
- The Fick's laws allow the quantitative appreciation of transfer process at microscopic level and make it possible the intervention for intensifying and establishing the optimum conditions for carrying it out.
- The phenomenological analysis of the main aspects from the friction area allows explication the peculiarities of the diffuse mass transfer.
- Very important parameters in mass transfer by diffusion and in temperature effect analysis are $D$ and $m$, which can be determined analytically or experimental and are depending on the used lubricant and local conditions of creation of the power transfer.
- The formed local area can be considered as a „membrane” of diffusion mass transfer and must have such properties, as the diffusion mass transfer may be possible.
- For the bronze/steel couple lubricated with glycerin, copper can diffuse from bronze, on the steel surface, forming through selective mass transfer a thin, superficial layer and with tribological performances.
- It is estimated that the variation of the thermal conditions, both in time, and in the near of the friction surface is the principal cause of the diffusion mass transfer, if lubricant film avoids copper oxidation from the selective layer, and this was demonstrated through the analytical calculation of the thickness transferred layer.
- The quantity of accumulated substance into a layer of known $h$, can be determined, if it accept a certain $g_s$ of the steel surface with copper from bronze, then can establish the correlation between the $h$ of this layer and the $g_s$ of the contact surfaces for the couple friction from steel/copper alloy.
- The thermal diffusion at selective mass transfer is a surface diffusion and this fact makes that the transfer of metallic particles (which it triggers in a relative short time) be depending the friction conditions (pressure, speed, temperature, and time).
- The friction conditions influence direct the thermal flow and his evolution, so that the diffusion mass transfer is an example of positive self-adjustable of the tribological phenomena.

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NOMENCLATURE:

$a$ – distance between two atomic equilibrium positions which are neighboring in the network (m);

$A$ – constant;

$A_c$ - contact area ($m^2$);

$c$ – constituents concentration ($kg/m^3$);

$D$ – diffusion coefficient ($m^2/s$);

$\overline{D}$, $\overline{D}_1$ and $\overline{D}_2$ - dimensionless parameter;

$D_0$ - frequency factor;

$D_1(\theta)$, $D_2(\theta)$, - diffusion parameter of the material 1 and 2, at the contact surface temperature ($m^2/s$);

$E_a$ = activation energy (J);

$g_s$ - saturation degree;

$g_r$ - relative saturation degree;

$h$ , $h_1$ – thickness (m);

$J$ – material flow, which diffuses and passes through the surface unit in time unit ($kg/m^2s$);

$k$ – constant;

$l$ – height (m);

$l_f$ - friction length (m);

$m$ - mass flow, which diffuses and passes through the surface unit in time unit ($kg/m^2s$);

$M_h$ - quantity of accumulated substance in the layer of thickness $h$ (kg);

$M_l$ - quantity of substance accumulated the whole body of height $l$ (kg);

$R$ – gas universal constant (J/molK);

$R_1$ – ray (m);

$t$ – time (s);

$T$ – temperature (K);

$v_a$ - relative sliding speed (m/s);

$z$ – direction (m), distance (m), coordination number of the network;

$\nu_0$ - vibration frequency of the atoms ($s^{-1}$);

$\theta$ - temperature (K).