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Influence of aging time and temperature on diffusion of alloyed copper

J. Konieczny [a,*], Z. Rdzawski [b], P. Bańbura [a], B. Preficz [a,c]

[a] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

[b] Institute of Non-Ferrous Metals, ul. Sowińskiego 5a, 44-100 Gliwice, Poland

[c] Institute of Polymer Materials and Dyes Engineering, ul. Chorzowska 50A, 44-100 Gliwice, Poland

* Corresponding e-mail address: jaroslaw.konieczny@polsl.pl

ABSTRACT

Purpose: The aim of this study is to determine the impact of aging time and temperature on the diffusion process of alloying elements inside alloyed copper CuCr0,7, CuFe2 and CuTi4.

Design/methodology/approach: It was assumed the activation energy for diffusion of small interstitial atoms is smaller than for large substitute atoms. To determine the influence of aging time and temperature on diffusion of alloying elements in binary copper-based alloys CuCr0,7, CuFe2 and CuTi4 it has been necessary to develop a suitable mathematical model. It has been shown that with the increase of time t, the diffusion pathway L is increased, but the impact of time is not as large as the effect forced by altering temperature. In general, multiple increase of time is equivalent to increasing the temperature by a few degrees.

Findings: The model should be used to estimate the average atom pathway of chromium, iron or titanium in copper matrix, caused by diffusion, and the diffusion path into the grain boundary without adsorption as a function of time and temperature aging

Research limitations/implications: The model should be used to calculate the influence of temperature and time of aging on the atoms diffusion pathway of the alloying elements in the selected alloyed copper types.

Practical implications: The results allow to calculate the average atom pathway L (with reasonable error level) for which the diffused atoms achieve the amount of free energy required to overcome the energetic barrier, on the basis of a combination of heat treatment parameters.

Originality/value: This paper presents the impact of the aging temperature on diffusion in the alloyed copper CuCr0.7, CuFe2 and CuTi4.

Keywords: Diffusion; Computational material science; Alloyed copper; Heat treatment

Reference to this paper should be given in the following way:

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ANALYSIS AND MODELLING

1. Introduction

Alloys of copper containing small additions of alloying element may be reinforced by the particles that form during the heat treatment [1-3]. Processes of precipitation inside titanium copper were thoroughly examined in reference to the classical heat treatment and kinetics of these processes is described in following papers [4-7]. After annealing preceding supersaturation, which aim was to dissolve the alloying component in the matrix, as a result of the aging process a new phase appears. It can be described as-β'-Cu_4Ti-β and is responsible for the effect of alloy strengthening.

In previous studies it has been proved that supersaturation is a critical and decisive process for determining the final microstructure and properties of CuTi alloys. Therefore, it is important to precisely define the influence of saturation conditions on the microstructure before introducing the next stage of treatment-aging [8, 9]. The above data shows that increasing the property is highly influenced by supercooling process, in particular the annealing time before cooling. Appropriately long annealing time should ensure complete dissolution of the alloying element in the matrix. For CuTi alloyed copper the titanium content affects hardness after supersaturation [10, 11].

The factor being decisive for defining the duration of both supersaturation and aging is the diffusion coefficient of alloying elements. It is determined by temperature, because the diffusion process is heat activated. The influence of temperature on diffusion coefficient of titanium in a copper matrix is described by Arrhenius equation, taking into account the probable error [12]:

$$D_{Ti/Cu} = \left(0{,}693^{+0{,}169}_{-0{,}135}\right)\times 10^{-4}\exp\left[-(196\pm 2)\frac{\frac{kJ}{mol}}{RT}\right]\frac{m^2}{s} \quad (1)$$

The activation energy of Ti diffusion at a temperature of 720-860°C for various phases: Cu4Ti, CuTi, Cu4Ti3 and the solubility of Cu(Ti) are respectively 192.2, 187.7 and 209.2kJ/mol, while for Cu(Ti), the activation energy grows linearly from 201.0kJ/mol up to 247.5kJ/mol with increasing concentration of titanium in the range of 0.5÷4.0% at.

Diffusion occurs by two main mechanisms: vacancy mechanism that takes place in substitution solutions; interstitial mechanism (interstitial solutions).

The condition for the occurrence of the vacancy mechanism is the presence of vacancies in the crystal lattice (which requires the delivery of adequate thermal energy) and overcoming the barrier of potential that surrounds atoms, which also requires adequate energy known as diffusion activation energy (Fig. 1). This energy is delivered by the thermal vibrations of atoms and consequently as the temperature rises the probability of atoms and vacancies switching positions increases exponentially. Each targeted stream of diffusing atoms is being accompanied by the opposite stream of vacancies.

There may also occur a specific mechanism of diffusion related to the presence of certain lattice defects such as dislocations and grain boundaries or as a consequence of the creation of compounds-reactive diffusion.

Since the diffusion in solids can be classified into [8, 9]:

- lattice diffusion (takes place in the crystal containing no linear or surface defects), which in this case can be skipped;
- volume diffusion (crystals containing dislocations),
- diffusion along the dislocation (pipe),
- diffusion along grain boundaries (boundary),
- surface diffusion (free surface of the crystal).

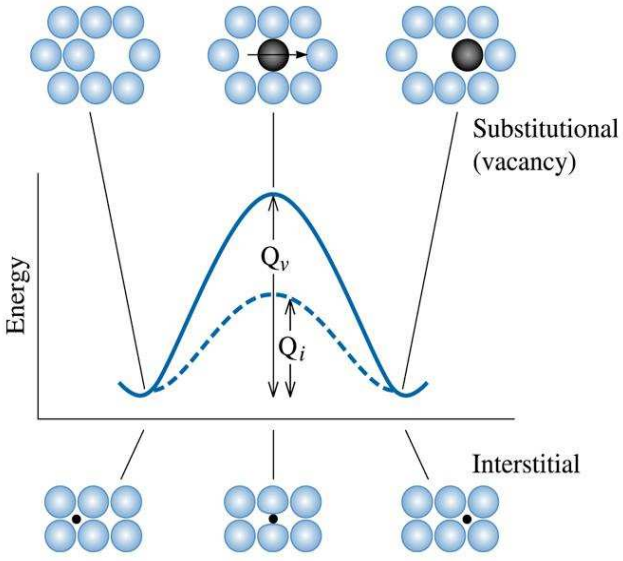

Fig. 1. Energy barriers for the diffusion of impurity atoms - substitute (vacancy mechanism - line), - interstitial (dashed line - Askeland) [13, 14]

On grain boundaries, the density of atoms packing is smaller than on the crystalline lattice which facilitates atoms' skipping. The higher the degree of atomic mismatch the lower activation energy for boundary diffusion becomes (the diffusion coefficient decreases), resulting in faster diffusion. The large-angled boundaries are the most effective ways of diffusion while the twin boundaries' are the least efficient.

Table 1.
Chemical composition of CuCr0,7 alloy

Cu	Cr	Zn	P	Pb	Sn	Mn	Ni	Sb	Bi	As	Cd
99.03	0.7	0.13	0.065	0.003	0.009	0.030	0.006	0.001	0.001	0.001	0.001

Table 2.
Chemical composition of CuFe2 alloy

Cu	Fe	Zn	P	Pb	Sn	Mn	Ni	Sb	Bi	As	Cd
97.53	2.34	0.13	0.065	0.003	0.009	0.030	0.006	0.001	0.001	0.001	0.001

Table 3.
Chemical composition of CuTi4 alloy

Cu	Ti	Zn	P	Pb	Sn	Mn	Ni	Sb	Bi	As	Cd
95.83	3.95	0.13	0.065	0.003	0.009	0.030	0.01	0.001	0.001	0.001	0.001

The grain boundaries, as a way of easy diffusion, get activated in the lower temperature range only (<about 0,8 T_{mlt}).

2. Material and experimental methodology

The initial material consisted of 3 kinds of copper alloys: Cu0.7, CuFe2 and CuTi4. The chemical composition is given in Tables 1-3.

Alloys underwent supersaturation: CuCr0.7 at temp. 1000°C/1h, CuFe2 at temp. 1000°C/1h and CuTi4 alloy at temp. 900°C/1h. In the next step, they were aged at 450, 500, 550 and 600°C for 1, 5, 15, 30, 60, 120 and 420 minutes. The resulting material was further examined.

The study was an analysis of the impact of temperature and aging time on the diffusion in studied alloys.

3. Results

The average atom pathway L for alloy CuTi4 resulting from diffusion, depending on the aging temperature calculated according to the equation (1) is:

$$L = \sqrt{Dt} \tag{2}$$

where:
L – the diffusion pathway [nm];
D – diffusion coefficient;
t – aging duration.

The calculated mean diffusion pathway L is the average distance over which the excited atoms diffuse thanks to the free energy required to overcome the energy barrier. The calculation results are presented in Fig. 2. The presented relation allows to deduce that the average distance covered by a titanium atom in the copper matrix caused by means of diffusion increases proportionally to changes of time and aging temperature.

Based on the approximation of calculated data a dependency between the diffusion pathway and aging time in fixed temperature could be determined. Approximated curves are defined by equations:

up to 450°C

$$L = 0{,}3745x^{0{,}5}$$

up to 500°C

$$L = 1{,}2769x^{0{,}5}$$

up to 550°C

$$L = 3{,}7512x^{0{,}5}$$

up to 600°C

$$L = 9{,}7399x^{0{,}5}$$

where:
L – the diffusion pathway [nm];
x – aging time.

The diffusion pathway along the grain boundaries without adsorption according to Fisher model can be determined by relation [15]:

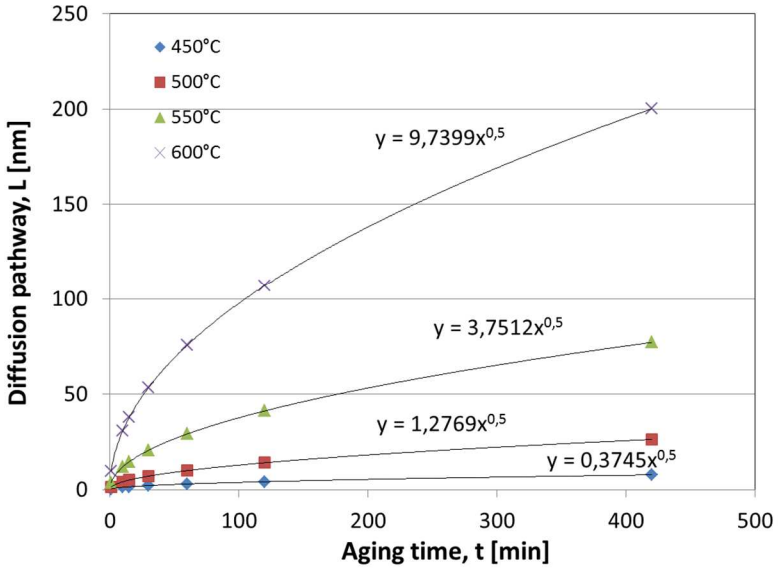

Fig. 2. The diffusion pathway of titanium in the alloy CuTi4 in relation to temperature and aging time [19]

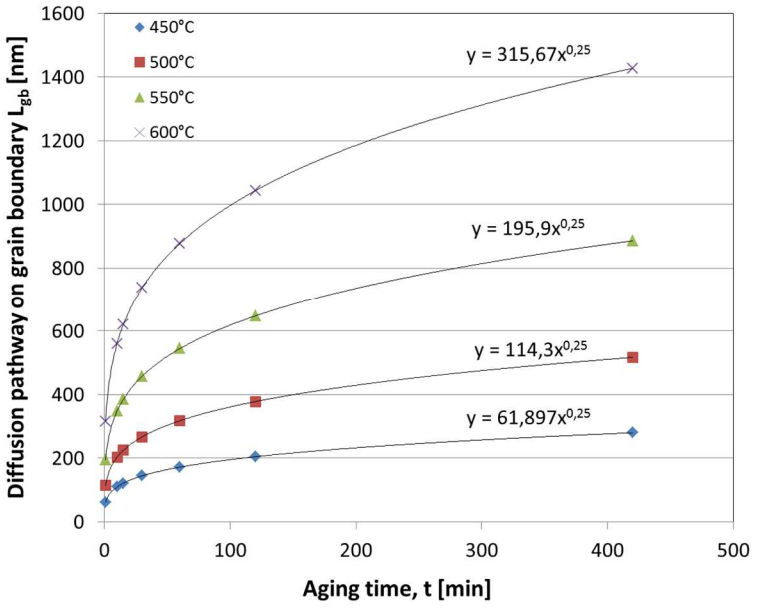

Fig. 3. The diffusion pathway along the grain boundaries without titanium adsorption in the CuTi4 alloy: relation between temperature and aging time [19]

$$L_{GB} = \sqrt{\frac{\delta D^{gz}\sqrt{\pi t}}{2\sqrt{D}}} \tag{3}$$

where:
δ – grain boundary width (usually $5*10^{-10}$ m);
D^{gz} – grain boundary diffusion coefficient;
t – time.

The grain boundary diffusion coefficient which is dependent on the border width, diffusion temperature, activation energy of diffusion and gas constant can be calculated using the following formula [16-18]:

$$\delta D^{gz} = 4 \times 10^{-13}\left(\exp\text{-}\frac{Q}{RT}\right) \tag{4}$$

Estimation of the diffusion activation energy Q in CuTi4 alloy was carried out, deriving from details presented in paper [12], regarding titanium content of 0; 0.5; 1 and 1.5%. This led to performing an linear approximation based on Pearson coefficient r=0.9958. Using the approximation equation, the value of diffusion activation energy Q could be calculated for CuTi alloy containing Ti concentrations of 4%, which turned out to be 228kJ/mol.

On the basis of above presented data the dependencies between diffusion pathway along the grain boundaries and aging time were defined (Fig. 3.).

Approximated curves are defined by following equations:

up to 450°C

$$L_{GB} = 61{,}897x^{0{,}25}$$

up to 500°C

$$L_{GB} = 114{,}3x^{0{,}25}$$

up to 550°C

$$L_{GB} = 195{,}9x^{0{,}25}$$

up to 600°C

$$L_{GB} = 315{,}67x^{0{,}25}$$

where:

L_{GB} – diffusion pathway on the grain boundaries [nm];

x – the time of aging.

The influence of aging temperature on the interdiffusion coefficient (reactive) of CuTi alloy depends on titanium concentration. The reactive diffusion increases with temperature growth for all the alloys with titanium concentration within range of 1.5-5.4% (Fig. 4).

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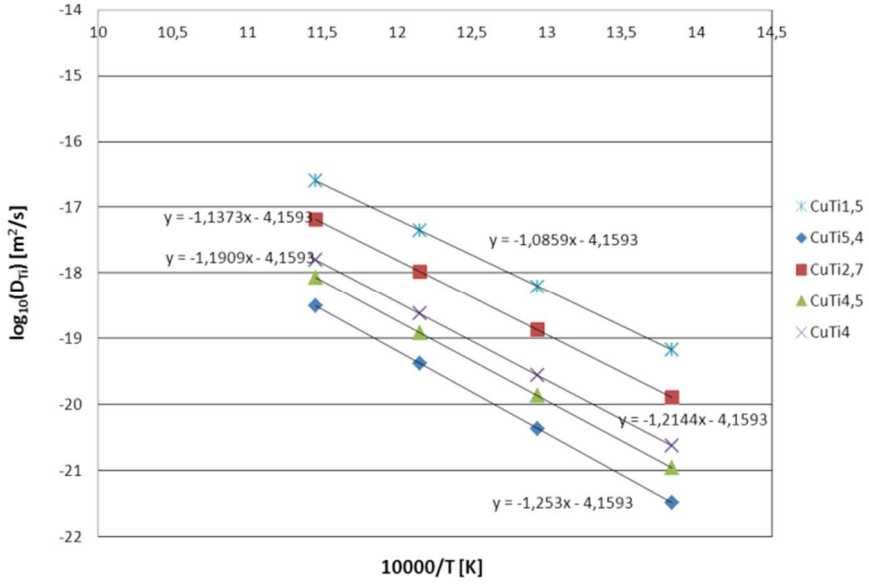

Fig. 4. The influence of temperature on the interdiffusion coefficient of alloyed copper CuTi based on experimental data [20-22]

Calculation results for diffusion enabled to define the average atoms pathway in CuTi4 alloy, depending on aging time and the pathway of diffusion on grain boundaries. In both cases the approximation allowed for determining equations dependent on the temperature of aging

For CuCr0,7 alloy the average diffusion pathway L of chromium atom, depending on the aging temperature, was calculated according to equation (2) and the diffusion coefficient of chromium in copper was achieved with equation (5):

$$D_{Cr/Cu} = 0{,}26 * 10^{-4} \exp\left(-\frac{1{,}99}{RT}\right)\frac{m^2}{s} \qquad (5)$$

Calculation results are presented in Fig. 5. The average diffusion pathway of chromium in the copper matrix caused by the diffusion comes from the achieved dependence and turns out to be increasing proportionally to aging temperature and time. However, the calculated values of L are lower for corresponding temperatures than for Ti diffusion in copper. Approximated curves are defined by equations:

up to 450°C

$$L=0.4064x^{0.5}$$

up to 500°C

$$L=2.5282x^{0.5}$$

up to 550°C

up to 600°C

$L=6.3543x^{0.5}$

$L=14.371x^{0.5}$

where:
L – diffusion pathway [nm];
x – aging time.

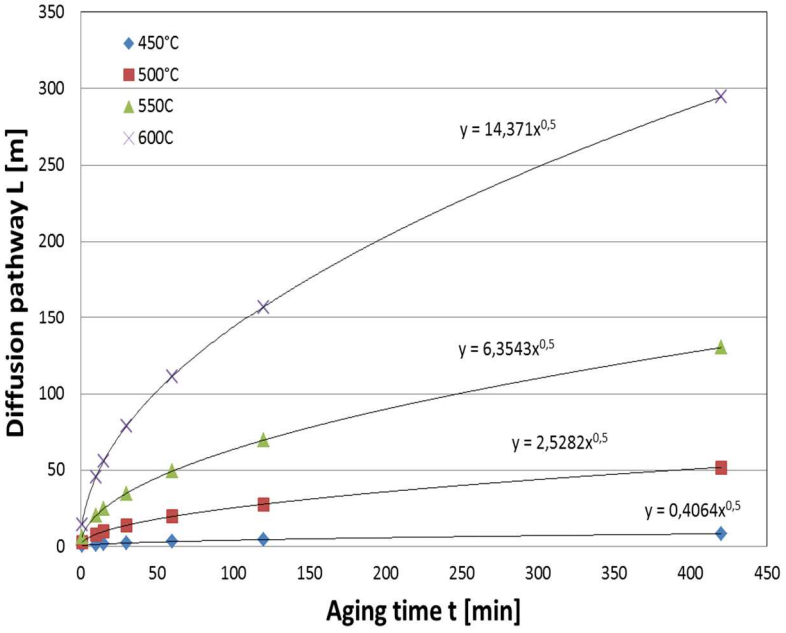

Fig. 5. The diffusion pathway of chromium in the alloy CuCr0,7 depending on temperature and aging time

Given this value, the dependence between the diffusion path into the grain boundary without adsorption and aging time at a specific temperature (Fig. 6) has been calculated by approximation. The approximated curves are defined by equations:

up to 450°C

$L_{GB}=25.458x^{0.25}$

up to 500°C

$L_{GB}=30.07x^{0.25}$

up to 550°C

$L_{GB}=49.005x^{0.25}$

up to 600°C

$L_{GB}=75.517x^{0.25}$

where:
L_{GB} – diffusion pathway on the grain boundaries [nm];
x – the time of aging.

Similarly, the average pathway L of the iron atom by diffusion in CuFe2 alloy, dependant on the aging temperature is calculated according to equation (2) while the diffusion coefficient for iron in copper was calculated by equation (5):

$$D_{Fe/Cu}=1{,}01\exp\left[-\frac{213{,}17\frac{kJ}{mol}}{RT}\right]\frac{cm^2}{s} \tag{6}$$

The calculation results are presented in Fig. 7. From the calculated relations, it follows that the mean distance covered by iron atom in copper matrix caused by diffusion elongates with increasing aging temperature and time. Approximated curves are defined by equations:

up to 450°C

$L = 0.0155x^{0,5}$

up to 500°C

$L = 0.0489x^{0,5}$

up to 550°C

$L = 0.1338^{0.5}$

up to 600°C

$L = 0.3266x^{0.5}$

where:
L – diffusion pathway [nm];
x – aging time.

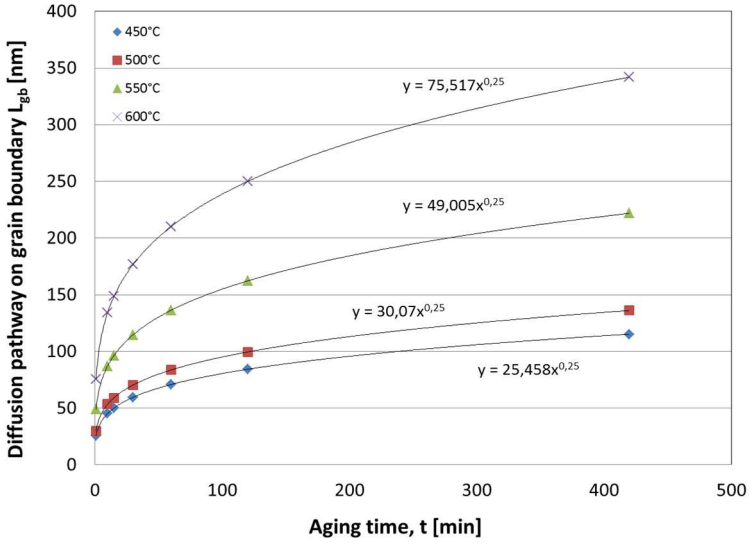

Fig. 6. The diffusion pathway on the grain boundaries without adsorption of chromium in the alloy CuCr0,7 depending on temperature and aging time

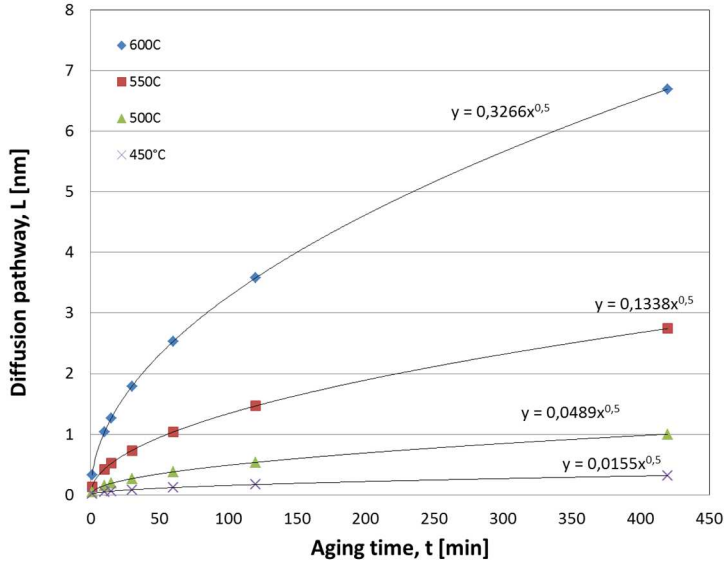

Fig 7. The diffusion pathway of iron in CuFe2 alloy, depending on temperature and aging time

The diffusion coefficient of activation energy Q for iron in copper equals 255.22 kJ/mol [23]. Substituting the value Q in formula (4) enabled calculation by approximation of the diffusion pathway in the grain boundary without adsorption in relation to aging time at a specific temperature (Fig. 8). Approximated curves are defined by equations:

up to 450°C

$$L_{GB} = 0.0999x^{0.25}$$

up to 500°C

$$L_{GB} = 0.2222x^{0.25}$$

up to 550°C

$$L_{GB} = 0.4487^{0.25}$$

up to 600°C

$$L_{GB} = 0.8257x^{0.25}$$

where:
L_{GB} – diffusion pathway on the grain boundaries [nm];
x – aging time.

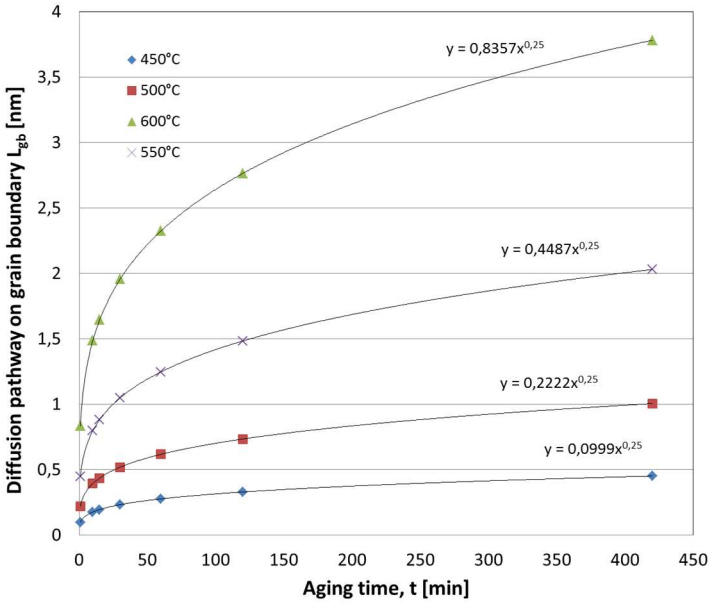

Fig. 8. The diffusion pathway along the grain boundaries without adsorption of iron in the CuFe2 alloy, depending on temperature and aging time

4. Conclusions

The diffusion of titanium, chromium and iron along grain boundaries in alloyed copper (without adsorption) enlarges with increasing the aging temperature. However, the bigger the diameter of atom, the further the diffusion pathway decreases. In case of titanium copper reactive diffusion increases with aging temperature growth and with inversely proportionally to titanium content.

With an increase of the time t, the diffusion pathway L increases, but the effect is not as large as for temperature. In general, multiple increase of time is equivalent to raising the temperature a few dozen degrees (Fig. 2, 5 and 7).

The diffusion activation energy for small interstitial atoms is lower than for large substitute atoms.

Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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