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# Kinetics of precipitation and recrystallisation of titanium copper

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## ABSTRACT

**Purpose:** The main aim of this work is to investigate effect of cold working following supersaturation of alloy copper in change in electrical conductivity of the finally aged CuTi4 alloy. Next, plots were worked out describing the kinetics of precipitation and recrystallisation from titanium copper, based on results of the electric conductivity measurements using the KJMA (Kolmogorov, Johnson, Mehl, Avrami) relationship.

**Design/methodology/approach:** The energy of the nucleation activation, precipitation, and grain growth was calculated by approximating the segments of the straight lines shown in the plots.

**Findings:** As a result of the electrical conductivity tests, the energy of the nucleation activation, growth, and precipitation of new particles during the ageing, was calculated for the two different variants of CuTi4 alloy processing.

**Research limitations/implications:** As a result of the electrical conductivity tests, and using the KJMA (Kolmogorov, Johnson, Mehl and Avrami) relationship, the energy of the nucleation activation, precipitations, and growth of new particles during the ageing, was calculated for two treatment variants.

**Practical implications:** It was found that the activation energy of nucleation of crystal nuclei is lower for the alloy treated according to variant 1st (supersaturation, ageing), while the activation energy of the precipitation and grain growth is lower for the alloy treated according to variant 2$^{nd}$ (supersaturation, cold working Z=50%, ageing).

**Originality/value:** Article presented  the energy of the nucleation activation, growth, and precipitation of new particles during the ageing, was calculated for the two different variants of CuTi4 alloy processing, based on the results of measurement of electrical conductivity.

**Keywords:** Alloyed copper; Heat treatment; Cold deformation; Precipitation; Recrystallisation

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## MATERIALS

## 1. Introduction

The analytical description of the microstructure recrystallisation process is based mostly on nucleation and grain growth, according to Kolmogorov [1], Johnson and Mehl [2], and Avrami [3,4], being commonly called the KJMA relationship. The analytical description of recrystallization kinetics based on this method is described in the literature as the Avrami equation:

$$y = 1 - \exp\left[-\left(kt^n\right)\right] \quad (1)$$

where:
y – transformation degree of the deformed metal,
k – transformation rate constant, $s^{-1}$,
t – time, s,
n – exponent.

This relationship has been formulated on the basis of assumptions concerning the model of nucleation, growth rate, and that the nucleation of new grains during recrystallization occurs uniformly within the deformed volume without taking into account the privileged places of crystallization [5]. The pronounced majority of authors of the contemporary publications assess the recrystallisation process using this relationship [6,7].

The goal of the work was to determine the energy of the nucleation activation, precipitation, and growth of grains in the technical CuTi4 alloy during ageing for two different treatment variants: 1$^{st}$ – supersaturation and ageing, and 2$^{nd}$ – supersaturation, cold working and ageing.

## 2. Material and methods

The starting material was an ingot from CuTi4 alloy hot rolled to thickness of 3.0 mm. Chemical composition is given in Table 1.

Table 1.
Chemical composition of CuTi4 alloy

| Concentrations of elements, % | | | | | |
|---|---|---|---|---|---|
| Cu | Ti | Zn | P | Mn | Ni |
| 95.82 | 3.95 | 0.13 | 0.06 | 0.03 | 0.01 |

The alloy was processed in two variants:

- 1$^{st}$ variant (supersaturation, ageing),
- 2$^{nd}$ variant (supersaturation, cold working Z=50%, ageing).

The same heat treatment conditions were applied in both cases. The test pieces were supersaturated from the temperature of 900°C in water after holding for 60 minutes in the chamber electric resistance furnace, and aged at the temperatures of 450, 500, 550, and 600°C for 1, 5, 15, 30, 60, 120,and 420 minutes.

Foerster Sigmatest device was used for electrical conductivity tests of the test pieces.

Transformation degree was calculated according to [8]:

$$y = \frac{\rho_0 - \rho_t}{\rho_0 - \rho(E_t)} \quad (2)$$

where:
y – precipitation process progress determined based on indirect measurements,
$\rho_0$ – electrical specific resistance of test pieces after supersaturation,
$\rho_t$ – specific resistance after the particular ageing time at a constant temperature,
$\rho(E_t)$ – electrical specific resistance for equilibrium conditions (for y=1), after the precipitation process in the structure was over.

The following data was prepared for calculations:
$\rho_0$ = 0.4 $\Omega mm^2/m$,
$\rho(E_t)$ = 0.083 $\Omega mm^2/m$.

Based on equation (2), the process progress y=0.6321 was calculated. Time constants (Tabs. 2 and 3) necessary for working out plots describing the kinetics of precipitation and recrystallisation in the investigated material were determined using equation (1).

Table 2.
Time constants for process progress y=0.6321 calculated according to equation (2) in the 1st treatment variant

| logt | Temperature T, °C | Time t, min |
|---|---|---|
| 0.96 | 450 | 9.2 |
| 0.87 | 500 | 7.5 |
| 0.87 | 550 | 7.5 |
| 0.66 | 600 | 4.6 |

Time-constant for y=0.6321. For cold rolled alloy after supersaturation time constants is shown in Table 3.

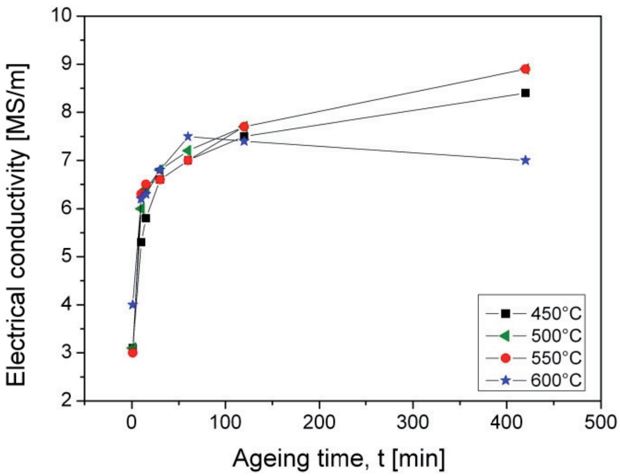
Table 3.
Time constants for process progress y=0.6321 calculated according to equation (2) in the 2nd treatment variant

| logt | Temperature T, °C | Time t, min |
|---|---|---|
| 1.15 | 450 | 14.1 |
| 1.02 | 500 | 10.5 |
| 0.42 | 550 | 2.6 |
| 0.61 | 600 | 4.1 |

## 3. Results and discussion

As a result of the tests performed, it was found that with increasing ageing time and temperature rise increases the electrical conductivity (for both treatment variants). This is due to the fact that during the ageing both β'-$Cu_4Ti$ and β-$Cu_3Ti$ phases particles precipitate. During the formation of these particles, titanium dissolved in the matrix diffuses from the substitutional positions of the supersaturated solid solution crystal lattice into the crystal lattice of the forming precipitates . Thus, conduction electrons are released which results in an increase in electrical conductivity. However, during ageing at 600°C, after 100 minutes, as the ageing is being extended, the electrical conductivity decreases (Fig. 1).

a)




b)

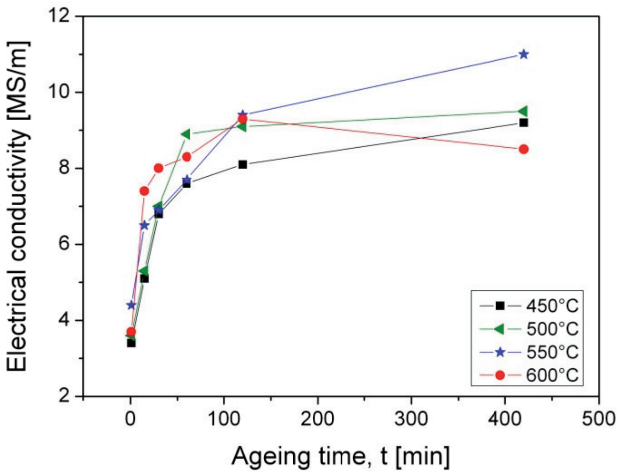



Fig. 1. Changes in electrical conductivity of CuTi4 alloy a) supersaturated and b) supersaturated and cold rolled, depending on the temperature and ageing time [9]

Based on the obtained results of the electrical conductivity the TTT diagram (Time-Temperature-Transformation) was worked out in which curves were plotted describing transformation kinetics for the supersaturated alloy, and aged next (1$^{st}$ variant), and for the supersaturated alloy, cold worked, and aged next – 2$^{nd}$ variant (Fig. 2). Transformation degree calculated for both CuTi4 alloy treatment variants is y=0.6321.

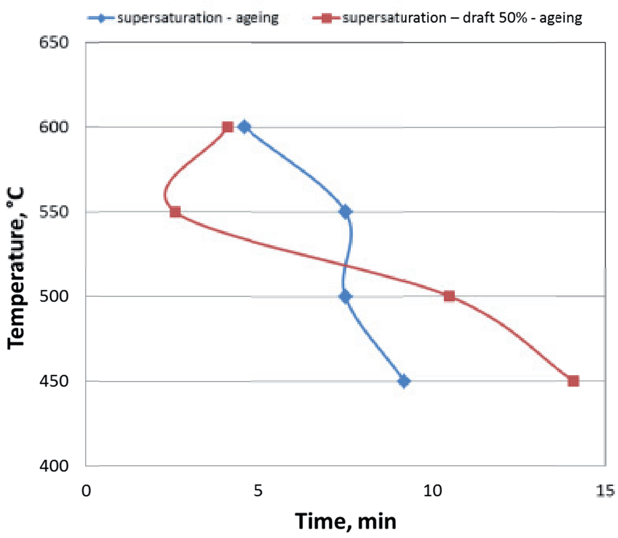



Fig. 2. TTT diagram describing transformation kinetics of CuTi4 alloy for transformation degree y=0.6321 [9]

Based on the results of electrical conductivity measurement the precipitation and recrystallization kinetics values were calculated for the investigated alloy using the KJMA relationship (1). Calculation results are shown using graphs (Figs. 3-6). As result of analysis of graphs, changes occurring in the microstructure were divided into three stages: nucleation of precipitations, precipitation of the second phase, and grain growth. In the case of the rolled alloy, precipitation process was superimposed also by the recrystallization process.

Comparing graphs characterizing the process of recrystallization and precipitation for both treatment variants one clearly see in the graph , the difference of slope of the relevant segments. This demonstrates the difference in the precipitation and recrystallization rates of the deformed and undeformed alloys (Figs. 3-6). The tables below contain the values of the activation energy of the subsequent transformation stages in the microstructure: nucleation Q1, precipitation Q2, and the grain growth Q3 (Tabs. 4-7). The results obtained are the approximate values which is due to the conditions of the approximation and also to the correlation results of straight lines with the results and are close to [10,11]. The values of activation energy is most likely dependent on the phase, whose nucleation, precipitation or growth takes place at a particular time [10, 11].

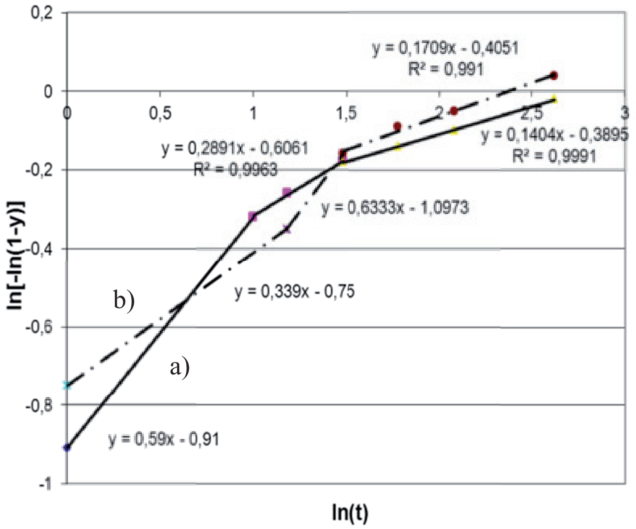



Fig. 3. Graphs of function ln[-ln(1-y )] versus lnt for CuTi4 alloy aged at temperature of 450°C, a) after supersaturation, b) after supersaturation and next cold working with draft Z=50%

Table 4.
The value of activation energy of the successive transformation stages in the CuTi4 alloy microstructure for the temperature of 450°C, calculated on the basis of Fig. 3

| Activation energy (kJ/mol) $Q_1$ – nucleation, $Q_2$ – precipitation, and $Q_3$ – grain growth | |
|---|---|
| For Z=0% | For Z=50% |
| $Q_{1Ti}$=87.4 | $Q_{1Ti}$=103.0 |
| $Q_{2Ti}$=103.9 | $Q_{2Ti}$=89.4 |
| $Q_{3Ti}$=131.7 | $Q_{3Ti}$=119.7 |

Table 5.
The value of activation energy of the successive transformation stages in the microstructure of the CuTi4 alloy for the temperature of 500°C, calculated on the basis of Fig. 4

| Activation energy (kJ/mol) $Q_1$ – nucleation, $Q_2$ – precipitation, and $Q_3$ – grain growth | |
|---|---|
| For Z=0% | For Z=50% |
| $Q_{1Ti}$=53.3 | $Q_{1Ti}$=146.4 |
| $Q_{2Ti}$=59.1 | $Q_{2Ti}$=102.7 |
| $Q_{3Ti}$=59.1 | $Q_{3Ti}$=206.2 |

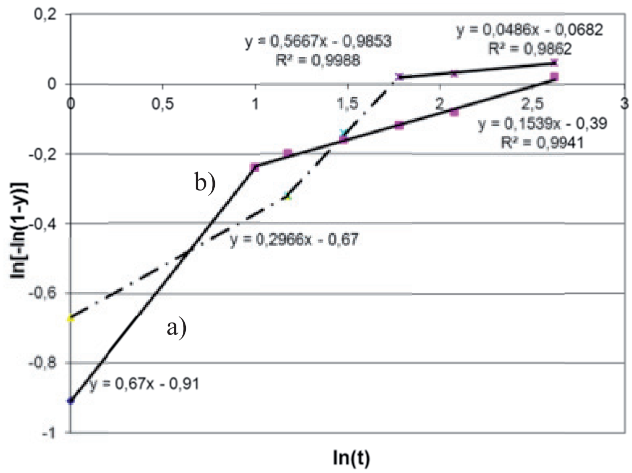



Fig. 4. Graphs of function ln[-ln(1-y )] versus lnt for CuTi4 alloy aged at temperature of 500°C, a) after supersaturation, b) after supersaturation and next cold working with draft Z=50%

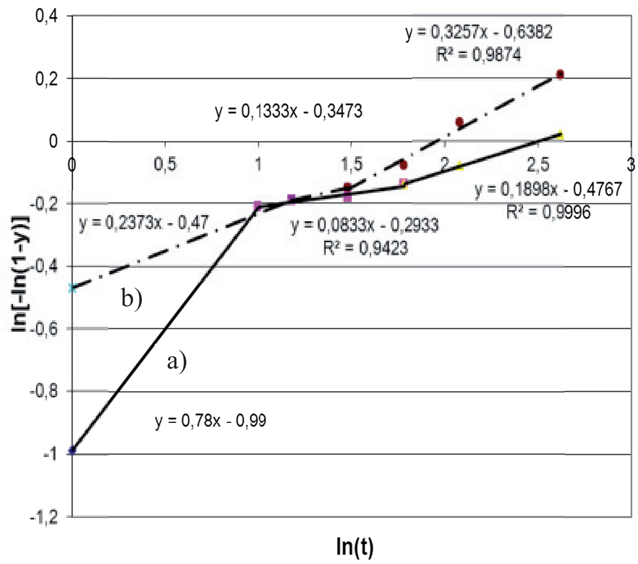



Fig. 5. Graphs of function ln[-ln(1-y )] versus lnt for CuTi4 alloy aged at temperature of 550°C, a) after supersaturation, b) after supersaturation and next cold working with draft Z=50%

## 4. Conclusions

It was found, therefore, based on the results of electrical conductivity test results that the CuTi4 alloy treated according to 2nd variant has a higher electrical conductivity (γ=11 MS/m)) than according to variant 1st (γ=9 MS/m).

Table 6.
The value of activation energy of the successive transformation stages in the microstructure of the CuTi4 alloy for the temperature of 550°C, calculated on the basis of Fig. 5

| Activation energy (kJ/mol) $Q_1$ – nucleation, $Q_2$ – precipitation, and $Q_3$ – grain growth | |
|---|---|
| For Z=0% | For Z=50% |
| $Q_{1Ti}$=92.8 | $Q_{1Ti}$=120.8 |
| $Q_{2Ti}$=189.5 | $Q_{2Ti}$=149.4 |
| $Q_{3Ti}$=135.4 | $Q_{3Ti}$=113.9 |

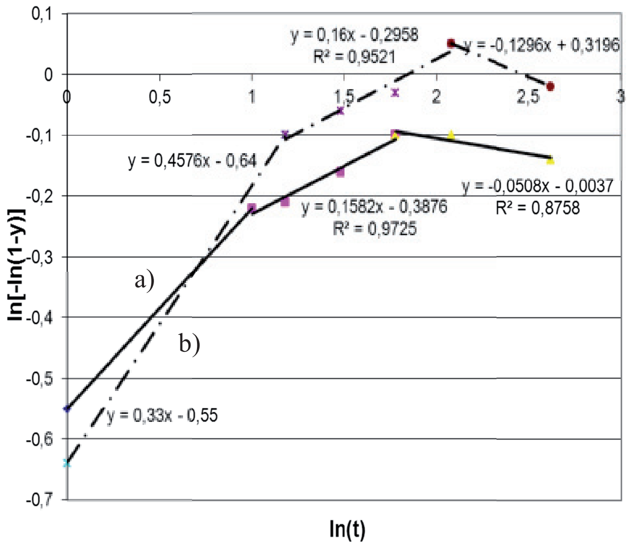



Fig. 6. Graphs of function ln[-ln(1-y )] versus lnt for CuTi4 alloy aged at temperature of 600°C, a) after supersaturation, b) after supersaturation and next cold working with draft Z=50%

Table 7.
The value of activation energy of the successive transformation stages in the microstructure of the CuTi4 alloy for the temperature of 550°C, calculated on the basis of Fig. 6

| Activation energy (kJ/mol) $Q_1$ – nucleation, $Q_2$ – precipitation, and $Q_3$ – grain growth | |
|---|---|
| For Z=0% | For Z=50% |
| $Q_{1Ti}$=115.7 | $Q_{1Ti}$=106.1 |
| $Q_{2Ti}$=148.7 | $Q_{2Ti}$=138.2 |
| $Q_{3Ti}$=189.9 | $Q_{3Ti}$=157,4 |

In both treatment variants, the highest conductivity is ensured by the final ageing at 550°C for 420 minutes, which is due to the process of precipitation of the second phase and collection of dopant atoms from the matrix to the precipitated particles.

As a result of the electrical conductivity tests, and using the relationship (2), the energy of the nucleation activation, precipitations, and growth of new particles during the ageing, was calculated for two treatment variants. It was found that the activation energy of nucleation of crystal nuclei is lower for the alloy treated according to variant 1st, while the activation energy of the precipitation and grain growth is lower for the alloy treated according to variant 2nd. The value of activation energy is most likely to depend on the phase concerned.

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