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Analysis of structural defect annealing in copper-base alloys exhibiting the shape memory effect

B. KOSTRUBIEC, J. RASEK, A. SALAMON, H. MORAWIEC
Institute of Physics and Chemistry of Metals, Silesian University, 40-007 Katowice, Bankowa 12, Poland
E-mail: kostrub@us.edu.pl

The process of martensite stabilization is investigated by resistometric method and positron annihilation spectroscopy in Cu-Al-Zn and Cu-Al-Ni alloys exhibiting the shape memory effect. A strong stabilization of martensite observed in Cu-Al-Zn alloys is explained by diffusion of divacancies and monovacancies formed during quenching with the following values of the Arrhenius relation $E_{2V}^{M} = (0.69 \pm 0.02)$ eV, $K_{04} = 6.4 \times 10^{8.0\pm0.1}$ s^{-1} and $E_{1V}^{M} = (0.84 \pm 0.02)$ eV, $K_{03} = 6 \times 10^{9.00\pm0.15}$ s^{-1}, respectively. It was found that the energy of vacancy formation in Cu-8.5Al-14.5Zn(%wt.) alloy was 0.56 eV. The proposed model has been confirmed by applying the positron annihilation technique. In Cu-Al-Ni alloys the disappearance of quenched-in vacancies is described by one recovery process only with the diffusion energy of monovacancy 0.74 eV. *© 2002 Kluwer Academic Publishers*

1. Introduction

The shape memory effect related to the reversible martensite transformation is observed, in Cu-Al-Zn and Cu-Al-Ni alloys. In order to obtain martensite phase alloys from the β or liquid phase were quenched. It is well known that this heat treatment leads to a relatively high concentration of quenched-in vacancies [1–4]. The above defects affect the course of reversible martensite transformation and are also responsible for the martensite stabilization effect observed in these alloys. It has been experimentally shown that diffusion of atoms in metals occurs primarily via the vacancy mechanism. Therefore studying the martensite stabilization and the instabilities of physical properties in copper alloys, the importance of the excess vacancies introduced during quenching should be taken into consideration.

The kinetics of different defects (point, linear and plane ones), their decay and redistribution in metals is described by the diffusion equations or as it was shown in papers [2, 5], by the following equation of chemical reaction rate:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -C^{\gamma} K_o \exp\left(-\frac{E_V^M}{k_B T}\right), \qquad (1)$$

where C is the concentration of the given type of defect, γ is the reaction order, K_o denotes the pre-exponential factor, E_V^M is the effective activation energy of migration, t denotes time, T is the absolute temperature, and k_B is the Boltzmann constant. The Equation 1 has two different solutions in respect to γ

$$\begin{cases} C = C_o \exp(-Kt) & \text{for } \gamma = 1, \quad (2a) \\ \dfrac{1}{C^{\gamma-1}} - \dfrac{1}{C_o^{\gamma-1}} = (\gamma - 1)Kt & \text{for } \gamma \neq 1. \quad (2b) \end{cases}$$

In Cu-Al-Zn alloys due to the low value of energy of vacancy formation a high concentration of excess monovacancies and divacancies appears at the ageing temperature T_a directly after quenching from a high temperature. In this case the kinetics of monovacancy decay (C_{1V}) and the kinetics of divacancy formation and their decay (C_{2V}) are described by the following kinetic model, i.e., through the set of differential kinetic equations [6, 7]:

$$\begin{cases} \dfrac{\mathrm{d}C_{1V}}{\mathrm{d}t} = -K_1 C_{1V}^2 + 2K_2 C_{2V} - K_3 C_{1V}, \\ \dfrac{\mathrm{d}C_{2V}}{\mathrm{d}t} = \dfrac{1}{2} K_1 C_{1V}^2 - K_2 C_{2V} - K_4 C_{2V}. \end{cases} \qquad (3)$$

The first expressions in the system of differential Equations 3 describe the process of divacancy formation, the second ones are responsible for the process of divacancy decomposition and the third ones for the process of monovacancy and divacancy annealing resulting in their decay. Kinetic constants of chemical reaction rates K_1, K_2, K_3, K_4 are expressed by the Arrhenius equations:

$$K_1 = K_{01} \exp\left(\frac{-E_{1V}^M}{k_B T}\right) \qquad (4a)$$

$$K_2 = K_{02} \exp\left(\frac{-(E_{1V}^M + B)}{k_B T}\right) \tag{4b}$$

$$K_3 = K_{03} \exp\left(\frac{-E_{1V}^M}{k_B T}\right) \tag{4c}$$

$$K_4 = K_{04} \exp\left(\frac{-E_{2V}^M}{k_B T}\right) \tag{4d}$$

where K_{oi} are pre-exponential factors that depend on entropy and the frequency of crystal lattice vibrations.

2. Investigated material

Investigations of the kinetics of structural defect decay were carried out for Cu-Al-Zn and Cu-Al-Ni alloys, and their chemical composition are given in Table I.

TABLE I Specification of chemical composition of the studied alloys

	Chemical composition in wt%			
Alloy designation	Cu	Al	Zn	Ni
Alloy I (bulk material)	77.58	8.04	14.38	–
Alloy II (bulk material)	83.00	13.00	–	4.00
Alloy III (melt-spinning)	83.00	13.00	–	4.00

Elements of 99.95% purity, subsequently melted in a vacuum furnace, were used to produce the alloys. Alloy III, obtained by means of the melt-spinning method at a wheel speed of $v = 12$ m/s, had the form of thin ribbon. Specimens for resistometric measurements were in the form of cubicoids 80 mm long, 5 mm wide and 1 mm thick for alloys I and II, and about 25–30 μm thick for alloy III. Specimens for positron annihilation spectroscopy measurements had the following dimensions 6 mm × 8 mm × 1 mm. In order to obtain the martensitic phase alloys I and II were quenched from $T_q = 1123$ K/30 min. to iced water and transferred immediately into the liquid nitrogen temperature. For alloy III the martensitic phase was obtained as a result of quenching from the liquid phase in the process of alloy forming. This alloy was then kept at room temperature.

3. Procedure

The method of positron annihilation and the resistometric method were used to study the kinetics of structural defect decay in investigated materials.

3.1. Positron lifetime measurement method

The lifetimes spectrum was measured in a conventional system of fast-slow coincidences. The positron source in the form of ^{22}Na in an envelope of a few-micrometer kapton foil was placed between specimens. Measurements were carried out for alloy I at room temperature immediately after quenching from 1123 K/30 min. to iced water and 24 hours after quenching. The time curves were approximated using the Gauss function. The lifetime spectrum was analysed by means of the LT computer programme [8], fitting the experimental curves with one or two components of the characteristic lifetimes.

3.2. Resistometric method

Measurements of electric resistivity were carried out by an automatic system using a four-point probe [7]. According to the Matthiessen rule the total changes of electric resistivity $\Delta\rho_t$ at the given temperature depend on the changes of residual resistivity $\Delta\rho_d$ and on the changes of resistivity $\Delta\rho_{pt}$ connected with $\beta_1' \Leftrightarrow \beta_1$ phase transformation [3]

$$\Delta\rho_t = \Delta\rho_d + \Delta\rho_{pt}. \tag{5}$$

Isothermal and isochronous curves of structural defects decay were measured at 77 K for specimens aged in the temperature area of martensitic phase existence lower $\beta_1' \Leftrightarrow \beta_1$ phase transformation. Hence, the total changes of resistivity connected with the scattering of conduction electrons on defects are given by Equation 6:

$$\Delta\rho_t = \Delta\rho_d \tag{6}$$

where the magnitude $\Delta\rho_d$ is proportional to the concentration of point, linear and plane defects. Measurements of electric resistivity at the temperature of liquid nitrogen have the following advantages:

a. they enable the observation of small intensity processes proceeding in the material,

b. the duration of the diffusion process (connected with defect decay) is much longer than the time of measurement.

4. Results of measurements

From the experiments performed [6, 7, 9, 10] it results that in copper alloys exhibiting the shape memory effect the structural defects play an important role in the course of reversible martensitic transformation. Therefore for Cu-Al-Zn alloys the kinetics of decay of excess point defects after quenching from the high-temperature β phase (alloy I) was analysed in detail. While for Cu-Al-Ni alloys the kinetics of decay of structural defects was analysed after quenching from the β phase (alloy II) and from the liquid phase (alloy III). For alloy II isochronous and isothermal resistivity curves were measured at the temperature of liquid nitrogen for specimens aged in the temperature range 273 K–390 K after quenching. A typical normalised isochronous resistivity curve and isothermal resistivity curve obtained at the ageing temperature $T_a = 323$ K for alloy II are shown in Fig. 1 and Fig. 2, respectively. In Cu-Al-Ni alloys after quenching from the high-temperature β phase the process of point defect decay is described by the solution (2a) with the reaction rate order $\gamma = 1$:

$$C_{1V} = C_{1V}^o \exp(-K_3 t), \tag{7}$$

where K_3 is the kinetic constant of chemical reaction rate for the process of monovacancy decay defined

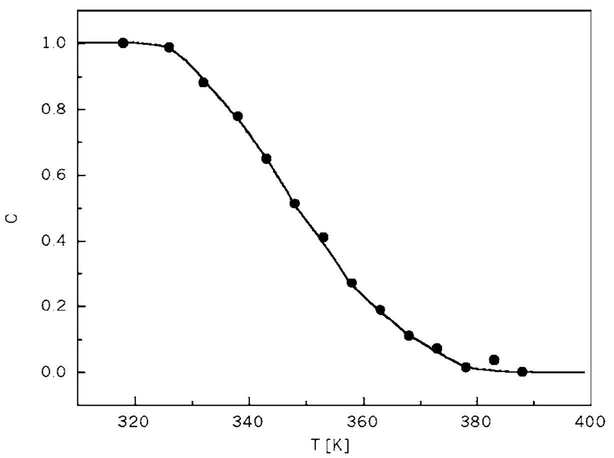

Figure 1 Normalised isochronous curve of electric resistivity for alloy II measured with the rate of step-heating $v = 5$ K/15 min. after quenching from 1123 K/30 min. Measurement of electric resistivity performed at the temperature of liquid nitrogen.

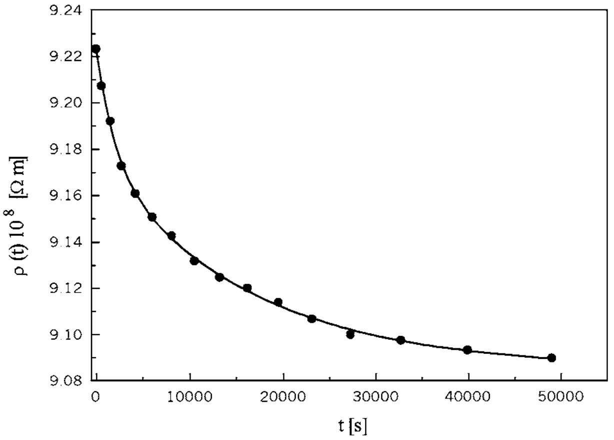

Figure 2 Curve of isothermal annealing at $T_a = 323$ K for alloy II immediately after quenching from $T_q = 1123$ K/30 min. Measurement of electric resistivity performed at the temperature of liquid nitrogen.

by Equation 4c and C^o_{1V} is the equilibrium concentration of monovacancies at the quenching temperature. In Fig. 3 shown the isothermal curve of electric resistivity at the ageing temperature 323 K in the co-ordinate system ln(C) versus t for alloy II. Using the Brinkman-Meechan method and the method of isothermal curve intersection the activation energy of migration for the process of monovacancy disappearance was determined. For alloy II the activation energy of vacancy migration was $E^M_{1V} = (0.74 \pm 0.08)$ eV and the pre-exponential factor of the Arrhenius relation was $K_{03} = 8 \times 10^{7.0\pm0.1}$ s^{-1}.

For alloy III after quick cooling from the liquid phase and long ageing at room temperature the isochronous and the isothermal resistivity curves were determined. A typical normalised isochronous resistivity curve measured at 77 K with the rate of step-heating $v = 5$ K/15min. for specimens aged in the temperature range 273 K–370 K is presented in Fig. 4. Fig. 5 shows isothermal resistivity curve obtained at the ageing temperature $T_a = 308$ K. For the studied alloy III an attempt was also made to describe the process of structural defect decay by means of a continuous spectrum. However, from the results obtained it is clear that the process of structural defect decay in alloy III may be described by means of a discrete spectrum with one reaction rate constant K_3 (see Equation 4c). The determined value of activation energy of migration was

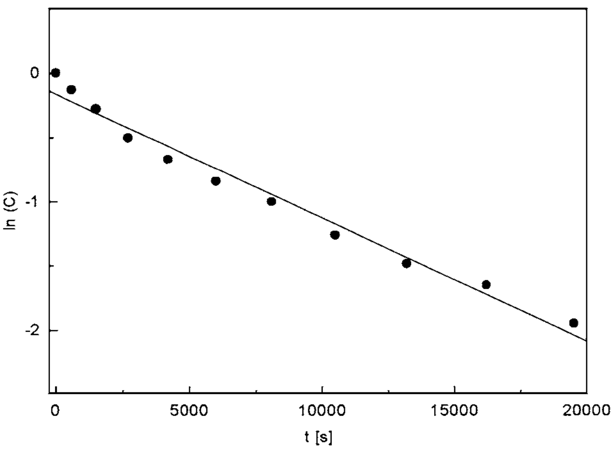

Figure 3 Isothermal curve of electric resistivity at 323 K in the co-ordinate system ln (C) versus t for alloy II.

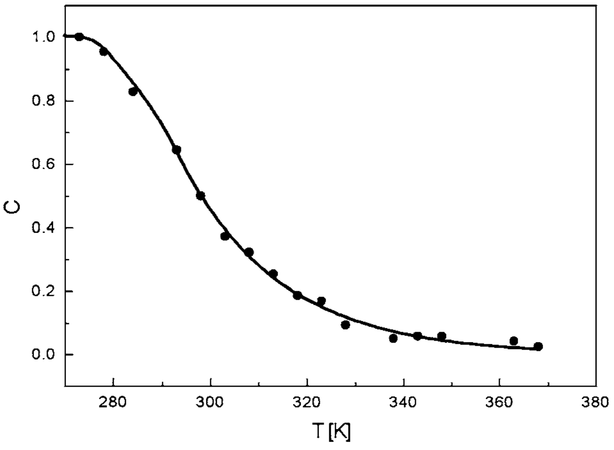

Figure 4 Normalised isochronous curve of electric resistivity for alloy III obtained by quick cooling from the liquid phase and long ageing at room temperature, determined with the rate of step-heating $v = 5$ K/15 min. Measurement of electric resistivity performed at the temperature of liquid nitrogen.

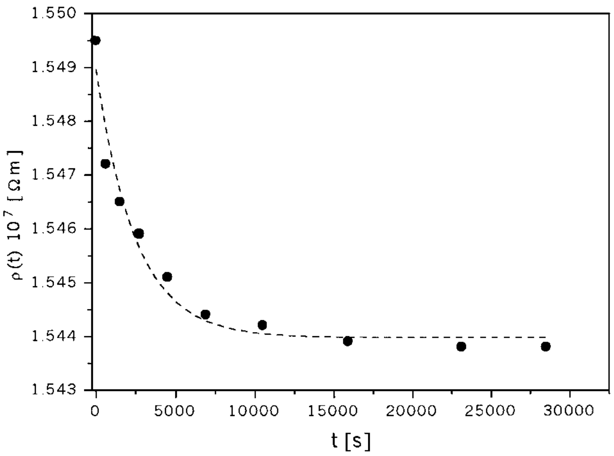

Figure 5 Curve of isothermal annealing at $T_a = 308$ K for alloy III after quick cooling from the liquid phase and long ageing at room temperature. Measurement of electric resistivity performed in liquid nitrogen.

$E^M_{1V} = (0.7 \pm 0.1)$ eV and the pre-exponential factor of the Arrhenius relation was $K_{03} = 1.7 \times 10^{8.0\pm0.3}\ \mathrm{s}^{-1}$.

The study performed for Cu-Al-Zn alloys [6, 7, 9, 10] has shown that after quenching from the high-temperature β phase a high concentration of vacancies appears. On the basis of the analysis of isothermal and isochronous curves of electric resistivity from Equation 1 two elementary processes of decay of excess vacancies have been distinguished in alloy I. The first process (A) with the order of reaction $\gamma = 2$ dominates in the short ageing periods is connected with the decay of divacancies. The second process (B) describing the disappearance of monovacancies (which occur for long ageing times) is characterised by the order of reaction $\gamma = 1$. Migration energies and pre-exponential factors were determined for both elementary processes using the Brinkman-Meechan method and the isothermal curve intersection method. The following values $E^M_{2V} = (0.69 \pm 0.02)$ eV, $K_{04} = 6.4 \times 10^{8.0\pm0.1}\ \mathrm{s}^{-1}$ and $E^M_{1V} = (0.84 \pm 0.02)$ eV, $K_{03} = 6 \times 10^{9.00\pm0.15}\ \mathrm{s}^{-1}$ were obtained for migration of divacancies and monovacancies, respectively. The temperature areas of monovacancy decay and their activation energy of migration are close to the temperature stages of electric resistance recovery for copper after quenching from high temperatures [4].

Since the process of vacancy decay in alloy I is complex, the application of a direct method for the determination of vacancy formation energy does not give satisfactory results here. In this alloy after quenching the resistivity changes connected with the decay of divacancies and monovacancies described by the sum of solutions of Equation 1 for $\gamma = 1$ (2a) and $\gamma = 2$ (2b) in the following form:

$$\Delta\rho_t = B_1 \frac{C^o_{2V}}{1 + C^o_{2V} K_4 t} + B_2 C^o_{1V} \exp(-K_3 t). \qquad (7)$$

In Equation 7 B_1 and B_2 are the coefficients of conduction electron scattering on divacancies and monovacancies, respectively, K_4 and K_3 are kinetic constants defined by Equations 4c and 4d. An example of decomposition of the normalised isothermal curve into two elementary processes at the ageing temperature $T_a = 333$ K is showed in Fig. 6. Numerical fitting of Equation 7 to experimental isothermal resistivity curves allows for the determination of the intensity of two processes and value of vacancy formation energy. For alloy I the energy of vacancy formation is $E^F_{1V} = (0.56 \pm 0.02)$ eV and the binding energy of vacancy pairs (divacancy) is $B = (0.11 \pm 0.02)$ eV. An experimental value of vacancy formation energy is comparable to the value obtained from the Fukushima-Doyama model [11] (the value is 0.645 for $e/a = 1.47$).

As it was mentioned above, the proposed model of disappearance of vacancies was additionally proved experimentally by applying the positron lifetime measurements. For the as quenched alloy I one component of the positron lifetime in divacancies $\tau_{2V} = (210 \pm 3)$ ps was obtained. A day later two components of the positron lifetime were observed in the spectrum, characteristic for annihilating positron in monovacancies $\tau_{1V} = (180 \pm 3)$ ps and in divacancies $\tau_{2V} = (210 \pm 3)$ ps.

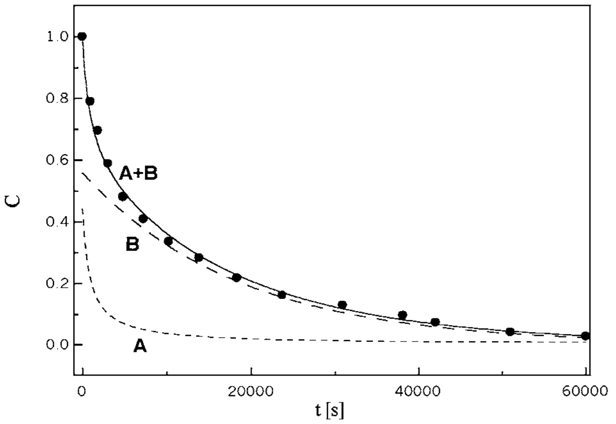

Figure 6 Decomposition of normalised isothermal curve of electric resistivity at 298 K into two elementary processes for alloy I. ● ● ● ●: experimental points (A): second-order process (A), (B): first-order process (B), (A + B): fitting with sum of processes (A) and (B).

5. Discussion of results

In as quenched copper alloys during the first cycle of transformation from the martensite phase into the parent phase, an increase in characteristic temperatures A_S and A_f (where A_S and A_f are the start and finish temperatures of reversible martensite transformation, respectively) is observed. This phenomenon in literature is called the stabilization of martensite. Different mechanisms are suggested to explain the effect of martensite stabilization: (1) changes in atomic arrangement within the martensite [12–14], (2) changes in the lattice parameters of martensite [14], (3) changes in the stacking faults density within a martensite plate [12, 13, 15] and (4) diffusion of structural defects (point, line and plane defects) [16–22]. The latter one seems to be important for Cu-Al-Zn and Cu-Al-Ni alloys. Results of earlier papers [6, 7, 9, 10] show that in Cu-Al-Zn alloys the effect of martensite stabilization is caused by monovacancies and divacancies present in the as quenched alloy. In Cu-Al-Zn alloys due to low energy of vacancy formation $E^F_{1V} = (0.56 \pm 0.02)$ eV a concentration of monovacancies is about 1×10^{-3} at. It is known that in alloys in which a high concentration of monovacancies occur, divacancies form. Therefore in Cu-Al-Zn alloys directly after quenching a high effect of martensite stabilization (an increase in A_s and A_f temperatures more than 200 K) may be explained by diffusion of divacancies and monovacancies during the first cycle of the reverse martensite transformation. Results obtained from resistometric measurements of the studied Cu-Al-Zn alloy are close to the ones obtained by the positron annihilation method. The lifetimes of positron trapped in divacancies and monovacancies received in our paper are in good agreement with the values given for Cu-Al-Zn alloys in [21]. The studies performed in [22] for the same alloys in thermodynamic equilibrium have also shown that in the temperature range 500 K–800 K positrons are trapped at monovacancies with a lifetime $\tau_{1V} = 182$ ps while above 800 K the lifetime of annihilating positrons in divacancies is $\tau_{2V} = 212$ ps.

The analysis of decay of point defects in alloys II introduced during quenching from the β phase has shown that diffusion of the excess vacancies runs by one elementary process with one activation energy of migration. It is well known that concentration of quenched-in vacancies mainly depends on energy of vacancy formation (E_{1V}^F). In Cu-Al-Ni alloy changes of resistivity ($\Delta\rho_t/\Delta\rho_o$) (proportional to the concentration of vacancies) are much smaller than changes in the Cu-Al-Zn alloy. This influences the martensite stabilization effect as well as the number of elementary processes responsible for the decay of quenched-in vacancies. For Cu-Al-Ni alloys after quenching from the β phase resistometric measurements show that a small effect of the martensite stabilization is observed, and the loops of the reversible martensite transformation are closed in the first measurement cycle. While in alloys III quickly cooled from the liquid phase the loops are open and are closed in the third measurement cycle only. For alloy Cu-Al-Ni obtained by the melt-spinning method (after a long period of ageing at room temperature) it was shown that disappearance of monovacancies is responsible for one elementary process with reaction order $\gamma = 1$. For this alloys the values of activation energy of monovacancy migration do not depend on the starting time of the measurement. In alloy II and alloy III of the same chemical composition differences in the characteristic temperatures of reversible martensitic transformation are observed, corresponding to the grain size. This result will be discussed in detail in our next paper.

6. Conclusions

1. In the investigated shape memory alloys the changes in the characteristic temperatures of the reversible martensite transformation are induced by mechanisms which speed up the diffusion processes (divacancies, monovacancies).

2. The number of elementary processes responsible for the decay of quenched-in vacancies during ageing in Cu-Al-Zn and Cu-Al-Ni alloys may be explained by the different values in the vacancy formation energy.

3. In Cu-Al-Ni alloys after quenching from the β phase and the liquid phase, the process of monovacancy diffusion is described by following values $E_{1V}^M = (0.74 \pm 0.08)$ eV, $K_{03} = 8 \times 10^{7.0\pm0.1}\ \mathrm{s}^{-1}$ and $E_{1V}^M = (0.7 \pm 0.1)$ eV, $K_{03} = 1.7 \times 10^{8.0\pm0.3}\ \mathrm{s}^{-1}$, respectively.

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