

The influence of ageing on the reversible martensitic transformation in Cu–Zn–Al alloys

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Abstract

The methods of internal friction and electrical resistivity were applied to study the influence of the ageing process of the martensite in two polycrystalline Cu–Zn–Al alloys on the course and variations of the reversible martensitic transformation. From the analysis of curves of $Q^{-1}=f(T)$ and the use of the chemical reaction rate equation, the activation energy for the initial stage of the martensite stabilization process $E=(0.73\pm 0.01)$ eV was determined; it corresponds to the disappearance of vacancies (alloy I). Based on the analysis of isochronal and isothermal curves of electrical resistivity, two processes (A and B) were distinguished (alloy II). Process A, with activation energy $E_A^M=(0.69\pm 0.02)$ eV, corresponds to the disappearance of divacancies, whereas process B, with activation energy $E_B^M=(0.84\pm 0.02)$ eV, corresponds to the disappearance of monovacancies.

1. Introduction

Practical application in technology of Cu–Zn–Al alloys exhibiting a reversible martensitic transformation is only possible when there is a stability of the physical properties and of the structure but above all when complete shape memory and stability of characteristic temperatures are ensured during extended use. The reversible martensitic transformation is markedly influenced by the changes in the real structure occurring during the low-temperature ageing process of the martensite and leading to its stabilization. In Cu–Zn–Al alloys the process of martensite stabilization can be enhanced by the high concentration of frozen vacancies formed during quenching from the high-temperature β phase and by the low energy value required for the formation of vacancies. From studies carried out hitherto, it seems that the stabilization process of the martensite in Cu–Zn–Al alloys is complex; the frozen vacancies formed during quenching and the process of atom ordering play a decisive role here [1–8].

In this work the methods of internal friction (IF) and electrical resistivity were applied to study the influence of the process of ageing of the martensite in Cu–Zn–Al alloys on the course and variations of the characteristic temperatures of the reversible martensitic transformation.

2. Experimental details

A study was made of two polycrystalline alloys with the following composition in at.‰: Cu–12.7 Zn–18.0

Al (alloy I) and Cu–12.4/Zn–17.2 Al (alloy II). Investigations were carried out on samples quenched directly from 1123 K in iced water and also on quenched samples with isothermal annealing at 398 K in order to lower the concentration of vacancies. As a result, the presence of martensite plates of the 18 R structure was observed. Next, the samples were subjected to the ageing process in the temperature range 297–343 K for various periods of time.

Measurements of the temperature dependence of internal friction were determined with the use of an audio frequency relaxator. Curves of $Q^{-1}=f(T)$ were determined in the temperature range 233–433 K with a deformation amplitude $\epsilon\approx 2\times 10^{-4}$, during heating and cooling of the sample.

Isochronal and isothermal curves of the electrical resistivity were determined in the temperature range 273–343 K with the use of the potentiometric method by applying the Diesselhorst compensator made by the Tettex company.

3. Results

As an example, Fig. 1 shows the temperature dependence of IF curves obtained for alloy I while heating aged samples at 297 K. It may be seen that the ageing process leads to broadening of the IF curves and to a shift of the temperatures of the martensite transformation. The curves of $Q^{-1}=f(T)$ during the cooling process and for the remaining ageing temperatures were

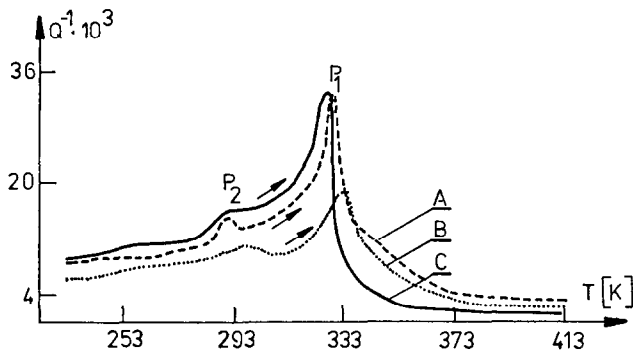


Fig. 1. Temperature dependence of IF obtained during heating of Cu-Zn-Al samples (alloy I) aged at 297 K for various time periods: A, 24 h; B, 7 days; C, 20 days; heating rate $V_h = 1.5 \text{ K min}^{-1}$.

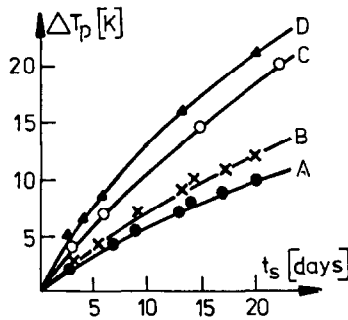


Fig. 2. Influence of the temperature and ageing time on the shift of the IF peak of the reversible martensitic transformation for alloy I: A, $T_s = 297 \text{ K}$; B, $T_s = 303 \text{ K}$; C, $T_s = 306 \text{ K}$; D, $T_s = 308 \text{ K}$.

obtained in an analogous way. From these curves the influence of the ageing process on the characteristic transformation temperatures changes was determined. In the initial stage of the ageing process, an increase of the temperatures of IF peaks was observed, corresponding to the reversible martensitic transformation and to the transformation of the matrix phase into martensite, together with a rise of the characteristic A_s, A_f, M_s, M_f temperatures (where: A_s , start temperature and A_f , finish temperature of the reversible martensitic transformation; M_s , martensite start temperature and M_f , martensite finish temperature). A marked prolongation of the ageing time leads in turn to a decrease and then again to an increase of these temperatures. The rise of the ageing temperature in the initial stage of this process induces an increase of transformation temperatures as a function of the ageing time (Fig. 2).

The dependences obtained indicate that the martensite stabilization process is thermally activated. Assuming that the shift of the reversible martensitic transformation temperature (ΔT_p) is connected with the change in defect concentration, an attempt was made to determine the activation energy of the martensite stabilization process from the equation of the chemical reaction rate:

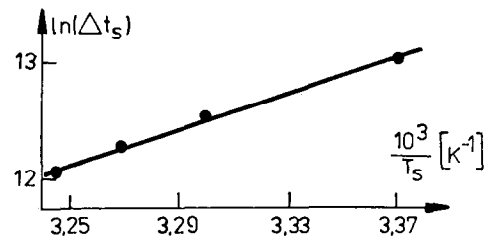


Fig. 3. Dependence $\ln(\Delta t_s) = f(1/T_s)$ obtained for $\Delta T_p = 7.5 \text{ K}$.

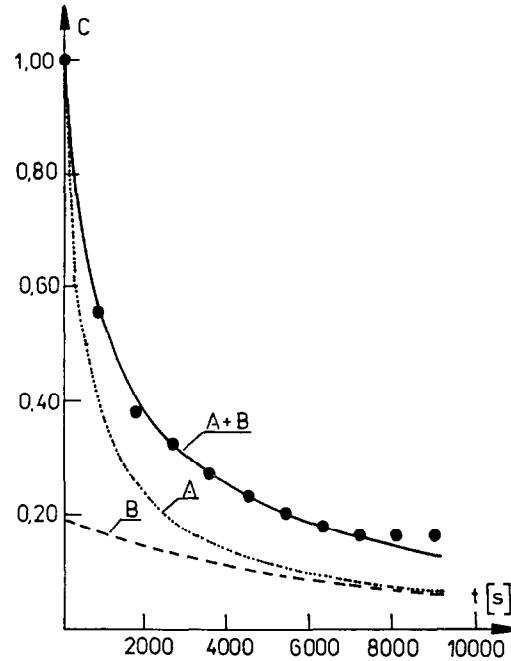


Fig. 4. Analysis of normalized isothermal curve of electrical resistivity obtained for alloy II at temperature 313 K; ●, experimental data.

$$\frac{d(\Delta T_p)}{dt} = -\Delta T_p^\gamma K \quad (1)$$

where γ is the order of reaction, and K is the reaction rate constant, which changes with the temperature of ageing, T_s , in conformity with Arrhenius' law:

$$K = K_0 \exp\left(\frac{-E}{k_B T_s}\right) \quad (2)$$

in which K_0 is the pre-exponential factor, E is the activation energy and k_B is Boltzmann's constant.

For the isothermal ageing curves the shift of the reversible martensite transformation temperature is a function of ageing time: $\Delta T_p = f(t_s)$. The activation energy can then be determined on the basis of the following dependence:

$$\text{const} = -\frac{E}{k_B T_s} + \ln(t_2 - t_1) \quad (3)$$

Making use of the determined curves of $\Delta T_p = f(t_s)$, the initial time of ageing and of the various ageing temperatures, E can be estimated for fixed values of ΔT_p from any section of these curves. For example, Fig. 3 shows the dependence $\ln(\Delta t_s) = f(1/T_s)$ for $\Delta T_p = 7.5$ K. When determining the slope of the obtained straight lines for various values of ΔT_p , the average value of the activation energy was $E = (0.73 \pm 0.01)$ eV.

In order to determine accurately the mechanism responsible for the martensite stabilization process, an analysis was carried out of the isochronal and isothermal curves of the electrical resistivity determined for alloy II, in which the ageing effects occurred with great intensity. For each curve obtained, two elementary processes (A and B) were distinguished (Fig. 4). Process A, occurring for a short time of ageing, has the reaction order $\gamma = 2$, while the other process B for a longer time period of ageing has the reaction order $\gamma = 1$. The following values were obtained for the activation energies: $E_A^M = (0.69 \pm 0.02)$ eV; $E_B^M = (0.84 \pm 0.02)$ eV.

4. Discussion

Studies carried out with the use of positron annihilation for alloy I showed that in the matrix phase the vacancies disappeared after quenching [9]. The estimated value of the martensite stabilization energy for the initial stage of the ageing process is near the value of the vacancy migration energy in the matrix phase. Hence the martensite stabilization process originated mainly from the disappearance of point defects formed by rapid quenching.

In alloy II the use of direct quenching from 1123 K to 273 K means that, as well as monovacancies, divacancies also exist. The annealing of the vacancies is described by a first-order reaction. Hence the elementary process B occurring for a longer annealing period should be linked with the disappearance of monovacancies. Process A, with the reaction order $\gamma = 2$, should be linked with the formation and the disappearance of divacancies.

The visible increase of characteristic temperatures and transformation temperatures in the initial stage of ageing is the result of the hindering of the motion of martensite plate boundaries by vacancies frozen during

quenching. Prolongation of the time of martensite ageing reduces the values of the transformation temperatures and characteristic temperatures caused by the change of the atom ordering of the martensite, whereas the stabilization process resulting in a renewed increase of characteristic temperatures is connected with the beginning of the precipitation of the equilibrium phases.

5. Conclusions

1. The stabilization process of Cu-Zn-Al alloys is heat-activated. For the activation energy of the initial stage of this process the following value was obtained: $E = (0.73 \pm 0.01)$ eV, which corresponds to the disappearance of vacancies (alloy I).

2. In the martensite stabilization process of Cu-Zn-Al alloys an important role is played by the vacancies introduced during quenching from the high-temperature β phase and by the atomic ordering of the martensite.

3. In Cu-Zn-Al alloy aged for a short time period a process occurs that is connected with the annealing of divacancies and has the energy $E_A^M = (0.69 \pm 0.02)$ eV, whereas for a longer period of ageing a process occurs with the energy $E_B^M = (0.84 \pm 0.02)$ eV, connected with the disappearance of monovacancies.

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