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Influence of point defects and grains size on the course of reversible martensite transformation in melt spun ribbons of the copper based alloys

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Materials

ABSTRACT

Purpose: In the paper Cu-Al-Ni-(Mn, Ti) alloys exhibiting the shape memory effect were studied. For the investigated alloys the characteristic temperatures of the reversible martensitic transformation, the influence of grains size and vacancy concentration on the course of the transformation were examined.
Design/methodology/approach: Using the resistometric method it was shown that the characteristic temperatures of the reversible martensite transformation strongly depend on the grains size.
Findings: For Cu-Al-Ni alloy the activation energy of migration of monovacancies and the pre-exponential factor of the Arrhenius equation were determined as $=(0.7\pm0.1)$eV, Ko$=1.7\cdot10^{\circ 8.0\pm0.3s-1}$, respectively.
Practical implications: The paper shows that the investigated alloys can be used as important functional or the so-called intelligent materials (actuators, sensors).
Originality/value: The parameters of the electronic structure - i.e. the coefficient of conduction electron scattering at grain boundaries, the mean free path, the coefficient of reflection of conduction electrons at grain boundaries, and the electrical resistivity for Cu-Al-Ni in the martensite and parent phase were determined.
Keywords: Martensitic transformation; Cu–based alloys; Melt –spun ribbons; Grain boundaries

1. Introduction

In recent years copper based alloys exhibiting the shape memory effect, obtained by fast cooling from the liquid phase are of an increasing interest [1-4]. According to results of a series of papers [1-2, 5-6] the characteristic temperatures of the reversible martensite transformation and also mechanical properties of these alloys strongly depend on grains size of the examined material. It is known that grains size of melt spun ribbons is considerably smaller than that of the bulk alloys with the same chemical composition. For example in paper [2] it was shown that for Cu-Al-Ni-Mn and Cu-Al-Ni-Mn-Ti alloys obtained by melt-spinning technique, the temperature M_s (start of the transformation from the parent phase into the martensite phase) depends on grains size according to the relation $\Delta M_S \propto d^{1/2}$, where ΔM_S is the difference between the temperature M_s of melt-spun ribbons (small grains) and bulk alloy (large grains) and d is the mean grain diameter.

The aim of the present paper is to determine the influence of the defect structure (vacancies, grain boundaries) on the characteristic temperatures of the reversible martensite transformation in cooper based alloys exhibiting the shape memory effect. Especially we are interested in: i) influence of grains size on the course of reversible martensite transformation, ii) the reflection and scattering coefficients of conduction electrons at grain boundaries, iii) diffusion parameters of vacancy migration in Cu-Al-Ni alloy (melt spun ribbons), and iv) the process of grain growth in Cu-Al-Ni alloy.

2. Experimental procedure

In the present paper two alloys exhibiting the shape memory effect were examined i.e. i) Cu-Al-Ni in the form of melt-spun ribbons (denoted as II/2) and as bulk material (II/1) and ii) Cu-Al-Ni-Ti-Mn in the form of melt-spun ribbons (I). The chemical compositions of these alloys are listed in Table 1.

Table 1.
Chemical composition of the examined alloys

Alloy	Chemical composition in wt %					Remarks
	Cu	Al	Ni	Ti	Mn	
I	80.1	11.9	5.0	1.0	2.0	melt-spun ribbon
II/1	83.0	13.0	4.0	-	-	bulk material
II/2	83.0	13.0	4.0	-	-	melt-spun ribbon

Specimens for resistometric measurements of bulk material (II/1 alloy) were in the form of cubicoids of dimensions 80 x 5 x 1 mm^3. The thickness of the melt-spun ribbons (I and II/2) was of about 25-30 µm. As received ribbons were in the martensitic phase, which is a result of fast cooling from the liquid phase. Measurements of electric resistivity (at 77 K, isothermal and isochronous curves) for samples aged in the temperature range of mertensitic phase (300 – 390 K) were carried out by an automatic system using a four-point probe [7]. Using this method for Cu-Al-Ni alloys with alloying additions of Mn and Ti the characteristic temperatures of the reversible martensite transformation ($\beta_1' \Leftrightarrow \beta_1$) were determined.

3. Results and discussion

3.1. Influence of point defects on time and temperature instabilities

For Cu-Al-Ni (II/2) alloy three consecutive cycles of the transformation $\beta_1' \Leftrightarrow \beta_1$ with a constant heating and cooling rate were determined by resistometric method. The course of reversible martensite transformation during heating and cooling at the first cycle is presented in Fig. 1. It was found that for the (II/2) alloy at the first two cycles the temperature hysteresis of the transformation $\beta_1' \Leftrightarrow \beta_1$ is open on low temperature side (points E - F, Fig. 1), and it closes just at the third cycle.

For Cu-Al-Ni (II/2) alloy the kinetics of decay of structural defects was analysed for samples after fast cooling from the liquid phase. Isochronous and isothermal curves of electrical resistivity were measured (at 77 K) for specimens aged in the temperature range 273K- 390K after fast cooling from the liquid phase. A typical normalised isochronous curve of electrical resistivity with the step-heating rate v=5K/15min. is presented in Fig. 2. It is proper to add that the normalised changes of electrical resistivity $\Delta\rho_n$ are proportional to concentration of vacancies. Fig. 3 shows normalised isothermal resistivity curve obtained for samples aged at temperature T_a= 308K.

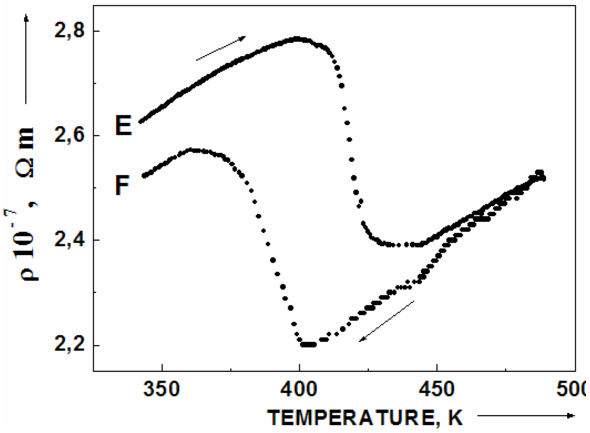

Fig. 1. Isochronous curve of electrical resistivity (in situ measurements) for Cu-Al-Ni (II/2) after fast cooling from the liquid phase during the first cycle of the transformation $\beta_1' \Leftrightarrow \beta_1$

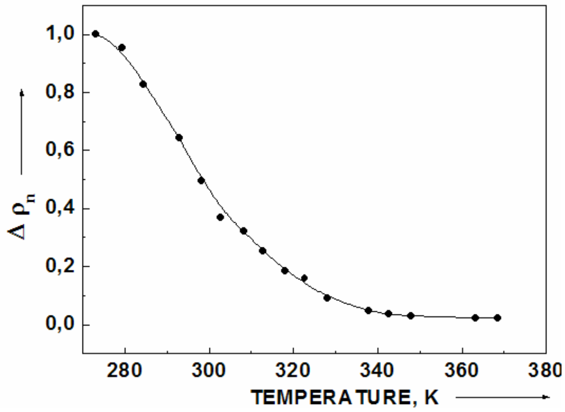

Fig. 2. Normalised isochronous curve of electrical resistivity (at 77K) for a melt spun ribbon of Cu-Al-Ni (II/2) alloy determined with the step-heating rate v=5K/15min

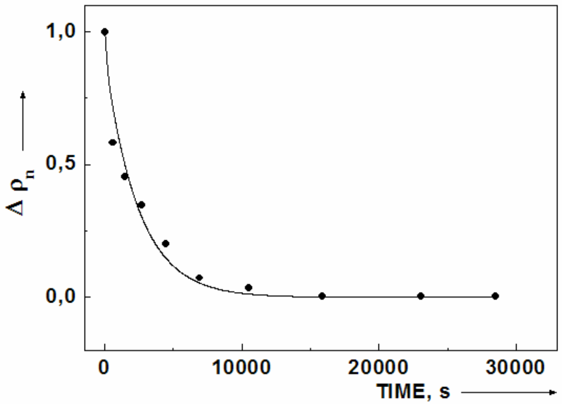

Fig. 3. Normalised isothermal curve of electrical resistivity (at 77K) obtained for melt spun ribbon of Cu-Al-Ni (II/2) alloy aged at T_a= 308K for

In copper alloys obtained by fast cooling from the liquid phase, martensite phase is obtained during the production process. According to the vacancy model of metals melting, the melting process begins when the crystal reaches a critical concentration of vacancies of about $3.7 \cdot 10^{-3}$ mole fraction. It is obvious that fast cooling from the liquid phase freezes large vacancy concentration [8, 9]. The presence of frozen vacancies influences time and temperature instabilities of physical properties (specific electrical resistance), and what follows the reversible martensite transformation. According to papers [10, 11] it is known that in Cu-Al-Zn alloys the effect of martensite stabilisation consisting in an increase of the characteristic temperatures A_s and A_f of the transformation from the martensite phase into the parent phase. For the examined alloy this is observed only during the first cycle of the transformation directly after quenching from the high-temperature β phase.

Resistivity changes at the points E - F (see Fig.1) are connected with a process of vacancy decay formed during the production process. Just like in bulk Cu-Al-Ni alloys, no increase in the characteristic temperatures A_s and A_f was observed [10]. The weak effect of martensite stabilisation observed in copper based alloys with the addition of Ni atoms can be explained by Fukushima-Doyama model [12]. According to this model and [10, 11] in alloys with the addition of Ni atoms, the energy of vacancy formation is much higher in relation to a copper based alloy with the addition of Zn atoms.

The changes of electrical resistivity measured versus time (see Fig. 3) show the decay of point defects frozen during production. Analysis of isothermal and isochronous curves by applying the Brinkman-Meechan method and the isothermal curves by using intersection method, indicates that within this temperature range vacancy migration can be described by a single exponential process. The kinetics of the process of vacancy decay in the examined alloy can be described by the equation of chemical reaction rate with the reaction order $\gamma=1$. The determined value of activation energy of migration of monovacancies for a spun-ribbon of Cu-Al-Ni (II/2) alloy is $E^{M}_{1V}=(0.7\pm0.1)$eV. The pre-exponential factor in the Arrhenius equation of is $K_o=1.7\cdot10^{8.0\pm0.3}s^{-1}$.

3.2. Influence of grain size on the course of reversible martensite transformation

The influence of grain size on the characteristic temperatures A_s, A_f, M_s, M_f was studied for Cu-Al-Ni-Mn-Ti alloy (I). This alloy was obtained by fast cooling from the liquid phase at the temperature T_m=1623K. Using this technique one can control the grains size by using different speed of cooling measured as the rotational speed of the drum turbine. In Table 2 the characteristic temperatures of the transformation $\beta_1' \Leftrightarrow \beta_1$ are shown.

In order to control the grains size samples of Cu-Al-Ni (II/2) alloy were annealed at temperature 1123K for 30min. In Table 3 the characteristic temperatures of the transformation $\beta_1' \Leftrightarrow \beta_1$ and the average grains size for the examinations alloys are listed.

In papers [1, 2] it was shown that in alloys obtained by fast cooling from the liquid phase characteristic temperatures A_S, A_f, M_S and M_f depend on grains size. From Table 2 it can be concluded that with increasing speed of fast cooling the grains size decreases and the start temperature of reversible martensite transformation shifts towards lower values. This dependence makes it possible to control the temperature range of the reversible martensite transformation thought the controlling parameters of the production process. It obviously enables wide application of the examined alloys. Let notice that changes in grains size of these alloys can be obtained in to ways: i) changing parameters of the production process and ii) application of a suitable thermal annealing of melt spun ribbons. From Table 3 it can be concluded that the average grain size in bulk alloy is of about two orders of magnitude higher than in the melt spun ribbons. The difference in grains size affects the temperature range of the reversible martensite transformation and changes the width of the temperature hysteresis of the phase transformation $\beta_1' \Leftrightarrow \beta_1$ (expressed by the difference between the temperatures A_f and M_f. Therefore in an alloy with a small grained microstructure the reversible martensite transformation takes place in a relatively wider temperature range in relation to an alloy with large grains size.

Table 2.
Characteristic temperatures of the transformation $\beta_1' \Leftrightarrow \beta_1$ for melt spun ribbons of Cu-Al-Ni-Mn-Ti (I) alloy; v is the rotational speed of the drum turbine (proportional to the speed of fast cooling) and d is the average grains size

Alloy	v [m/s]	d [μm]	T_m [K]	A_s [K]	A_f [K]	M_s [K]	M_f [K]
I/1	12	5.5	1623	380	410	360	320
I/2	19	4.5	1623	340	390	330	280
I/3	26	4.0	1623	320	360	320	270

Table 3.
Characteristic temperatures of the reversible martensite transformation of melt spun ribbons of Cu-Al-Ni (II) alloy, bulk alloy and melt-spun ribbons annealed at T_a=1123 K/30min.

Alloy	d [μm]	A_S [K]	A_f [K]	M_S [K]	M_f [K]	A_f-M_f [K]
Bulk alloy (II/1)	450	440	451	431	414	37
Melt-spun ribbons (II/2) after annealing at T_a=1123K/30min. and fast cooling to 273K	23	425	440	422	395	45
Melt-spun ribbons (II/2) in the as received state	4	410	430	422	375	55

3.3. The process of grain growth in Cu-Al-Ni alloys

Fig. 4 shows d^{-1} (where d is the mean grains diameter) plotted versus temperature of isothermal annealing for 1800s. According to [13], d^{-1} is directly proportional to concentration of surface defects S_v. The data presented in Fig. 4 allows controlling grains size of the examined alloy through application of an appropriate

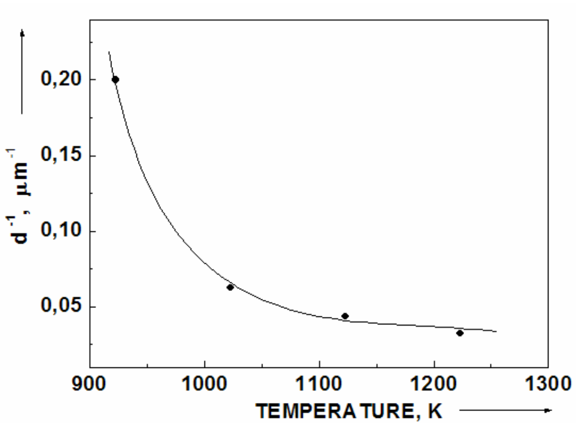

Fig. 4. Dependence of the inverse grains diameter ($d^{-1} \sim S_v$) versus annealing temperature for Cu-Al-Ni (II/2) alloy obtained by fast cooling from the liquid phase

isothermal annealing. The grain growth controlled in this way enables wide application of Cu-Al-Ni alloys with a concrete chemical composition.

Examination of Cu-Al-Ni bulk alloys and melt spun ribbons showed significant changes in electrical resistivity and differences in average grains size. From these facts one can conclude that the concentration of surface defects S_v in both alloys is also significantly different. In Table 4 the total changes in electrical resistivity (ρ) and the average grains size determined for bulk Cu-Al-Ni (II/1) alloy and melt-spun ribbons (II/2) after additional annealing are listed.

Table 4.
The average grains size and electrical resistivity (measured at room temperature ρ_{rt} and at 77 K ρ_n), coefficients R_R, and Z for bulk Cu-Al-Ni (II/1) alloy, melt spun ribbons of alloy (II/2) after annealing at temperature T_a= 1123K/30min.

Alloy	d [µm]	$\rho_{rt} \cdot 10^{-7}$ [Ωm]	$\rho_n \cdot 10^{-7}$ [Ωm]	$R_R = \frac{\rho_{rt}}{\rho_n}$	$Z = \frac{1}{R_R - 1}$
Bulk alloy (II/1)	450	1.61	1.12	1.59	1.69
Melt-spun ribbon (II/2) after annealing at T_a=1123 K/30min. and quenching to 273 K	23	2.07	1.36	1.53	1.89
Melt-spun ribbon (II/2) in the as received state	4	2.08	1.41	1.47	2.13

Making use of the measurements of the total electrical resistivity, one can determine the coefficient of conduction electron scattering at grain boundaries k_{GB} defined as [13-14] as:

$$\rho_c = \rho_o + k_{GB} S_V \qquad (1)$$

where: ρ_o is the electrical resistivity of a monocrystal. The quantity k_{GB} can be expressed by the parameters of the electronic structure of metal: the mean free path (l_o), the Fermi surface (S_F), and the coefficient of reflection of conduction electrons at grain boundaries (R) [13, 15]:

$$\begin{cases} \rho_c = \rho_o + \dfrac{3}{4}\rho_o l_o \dfrac{R}{1-R} S_V \\ \rho_c = \rho_o + \dfrac{9\pi^3 \hbar}{e^2 S_F} \dfrac{R}{1-R} S_V \end{cases} \qquad (2)$$

where: e is the electron charge, $\hbar$ is the Planck's constant divided by 2π.

In Table 5 the parameters of the electronic structure of metal (l_o, R, k_{GB}, ρ_o) obtained for Cu-Al-Ni (II) alloy in the martensite phase (at 77 K) and in the parent phase (at 473K) are listed. Additionally the values for pure copper determined in papers [13, 15] are also included.

Table 5.
The values of the coefficient of conduction electron scattering at grain boundaries k_{GB}, the mean free path (l_o), the coefficient of conduction electron reflection at grain boundaries (R), and electrical resistivity (ρ_o) for Cu-Al-Ni (II), and for pure copper [13,15]

Alloy	k_{BG} [Ω m^2]	$l_o \cdot 10^{-9}$ [m]	R	$\rho_o \cdot 10^{-8}$ [Ω m]
Cu-Al-Ni				
at 80K martensitic phase	$3.14 \cdot 10^{-14}$	4.39	0.987	12.0
at 473K parent phase	$1.64 \cdot 10^{-13}$	3.89	0.997	13.5
Pure cooper				
at 80K	$2.82 \cdot 10^{-16}$	350	0.350	0.194

4. Conclusions

4.1. The characteristic temperatures of the reversible martensite transformation in copper based alloys strongly depend on grains size and can be controlled in two ways: i) by changing parameters of the production process i.e. fast cooling rate and ii) application of a suitable thermal annealing of melt spun ribbons.

4.2. The diffusion parameters of vacancy decay in melt spun ribbons of Cu-Al-Ni alloy are E_{1V}^{M}=(0.7±0.1) eV and $K_o = 1.7 \cdot 10^{8.0 \pm 0.3} s^{-1}$.

4.3. The reflection and scattering coefficients of conduction electrons at grain boundaries in Cu-Al-Ni alloy are higher in relation to pure copper. The mean free path of conduction electrons in Cu-Al-Ni alloy are about two orders of magnitudes lower than the l_o for pure copper.

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