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Thermodilatometry investigation of the martensitic transformation in copper-based shape memory alloys

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Abstract

The characteristic temperatures and kinetics of the martensitic and reverse transformation in the copper-based shape memory alloys were examined on the base of the differential thermodilatometry (DTD) measurements. The values of activation energy at different heating and cooling rates were determined by the Kissinger and Ozawa methods. © 1997 Elsevier Science B.V.

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1. Introduction

Shape memory alloys have appealed a lot in recent years as new special materials of unusual macroscopic features that make them interesting for study and research as well as for their possible application in techniques, power plants and space technology [1–3].

Shape memory refers to the ability of certain plastic deformed metals and alloys to regain their original shape during the heating process due to complete or almost complete absence of deformation [4,5].

Shape memory effect has been studied for many binary and ternary alloys, as well as for some pure metals [4,5]. However, investigations have shown [5–7] that wide application can be found only for nitinol and copper-based alloys that show shape memory effect.

Copper-based alloys, compared to Ni–Ti alloys, possess somewhat lower mechanical properties due to their larger grain size and elastic anisotropy [6,8]. On the other hand, copper-based alloys can be produced more easily and more economically [9,10], which makes them cheaper compared to Ni–Ti alloys, whose production technology and processing are expensive and complicated [11]. Also, their application in various fields is wide [4,5,7] and it is expected that the application of copper-based alloys exhibiting shape memory effect, shall be even wider in future, because of the acceptable price of material and simpler fabrication.

The basis for the achievement of shape memory effect is presented [12] by the martensite crystal structure. This structure is possible to achieve by two basic methods [4]:

- by subjecting the alloy to a stress whose force is proportional to temperature; or

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- by rapid quenching of alloy to some critical temperature.

By application of the second method, which is more widely applied, martensite structure occurs [4] spontaneously by shearing motion of the atoms in the alloy or by nucleation and crystal process growth.

The heating process causes restoration of crystals in high-temperature phase (called beta or parent phase) [5] and the removal of plastic deformation. Concurrently, all physico-mechanical properties are restored. During the shape recovering process, the alloys can produce a displacement or a force, or combination of the two, as a function of temperature [5].

Accordingly, the essence of shape memory depends on the capability of alloys to undergo the so-called thermoelastic martensitic transformation [13–15].

Thermoelastic martensitic transformation is achieved by the formation of martensite and grows continuously with the decrease of temperature and increase of stress, and decreases continuously, becoming smaller according to the same curve with the increase of temperature or decrease of stress [15].

Thermoelastic martensitic transformation is characterized by the following temperatures [4,5]:

- M_s – the temperature at which martensite starts to transform into the high-temperature (parent) phase;
- M_f – the temperature at which martensite finishes to transform into the high-temperature (parent) phase;
- A_s – the temperature at which the high-temperature (parent) phase starts to transform into the martensite; and
- A_f – the temperature at which the high-temperature (parent) phase finishes to transform into the martensite.

Depending on mutual relationship of temperatures A_s and M_s, thermoelastic martensitic transformation may be of the following order [4]:

- first order ($A_s > M_s$), i.e. $A_f > A_s > M_s > M_f$; and
- second order ($A_s < M_s$), i.e. $A_f > M_s > A_s > M_f$.

Investigations made so far, related to copper-based shape memory alloys, apart from the description of production technology, are mainly based on investigation of the structure of martensite, observations and prevention of negative effects on the shape memory process, reversibility and cyclic recurrence of martensitic transformation [5,16].

A smaller number of works deal with the definition of temperatures of martensitic transformation, which are significant for shape memory process in copper-based alloys.

For this reason, investigation of Cu–Zn–Al alloy is carried out by the method of dilatometry [17] with the aim of defining not only temperatures of the start, finish and maximum of martensitic and reverse transformation at various heating and cooling rates, but also to include TD method along with other, classical methods of investigations such as DTA and DSC as presented in this paper.

Besides, kinetic parameters related to shape memory process have been determined by the methods of Kissinger [18] and Ozawa [19].

2. Experimental

All experimental investigations are carried out with oxygen-free copper, pure metallic zinc and aluminium of p.a. grade.

The Cu–Zn–Al alloys are obtained [20] by melting the charge that is prepared of oxygen-free copper, pre-alloy of Cu–Zn (Zn 49.23%) and pre-alloy of Cu–Al (Al 48.16%). Charge melting is carried out in a gas pot furnace. Alloys are cast into moulds of dimensions 14×65×100 mm^3. After preparation of external surfaces, laths of dimensions 5×50 mm^2 are cut, which are used for TD investigations.

Chemical compositions of obtained alloys are shown in Table 1.

With the aim of forming the martensite structure, in the referred alloys, the cooling process is carried out from the β-phase region, the obtained laths are heated for 10 min at 850°C and then quenched in water.

Table 1
Alloy compositions

No.	Composition/wt%		
	Cu	Zn	Al
I	78.97	15.75	5.28
II	68.84	27.60	3.51

TD investigations of samples prepared in the described manner are carried out on the electronic dilatometer 402 E at high temperatures (Netzsch, Germany) with molybdenum pipe furnace and a protective gas atmosphere of nitrogen and hydrogen.

The differential thermodilatometry (DTD) curves, obtained by simultaneous TD–DTD instruments, are used for processing the obtained results.

Experiments are carried out at various heating and cooling rates of 3, 5, 10, 15 and 20 K min^{-1}.

3. Results and discussion

Simultaneous TD–DTD method is used for determining the temperatures of martensitic and reverse transformation, at various rates of heating and cooling, and for determination of the process kinetic parameters related to shape memory effect in the ternary Cu–Zn–Al system.

The obtained peaks for the two different alloy compositions during heating are shown in Fig. 1 and during cooling in Fig. 2.

Temperature of the start, finish and maximum transformation of martensite into parent phase at various heating rates (reverse transformation) as well as the temperatures of the start, finish and maximum transformation of parent phase into martensite at various rates of cooling (martensitic transformation) are read from the obtained DTD curves.

The obtained data is presented in Table 2.

The obtained DTD peaks and characteristic temperatures serve as a basis for determining kinetic parameters, i.e. activation energy of the process of martensitic and reverse transformation.

Since various rates of heating and cooling are used for determining activation energy, the methods of Kissinger and Ozawa lead to linear relationships for martensitic and reverse transformation as well.

In Table 2, the results are processed according to the method developed by Kissinger [18]:

$$\ln[\phi/T_m^2] = C - E/RT_m \tag{1}$$

and Ozawa [19]:

$$\ln\phi = C_1 - E/RT_m \tag{2}$$

where ϕ is the heating rate, T_m the maximum on the DTD peak, E the activation energy, R the universal gas constant and C and C_1 the integration constants.

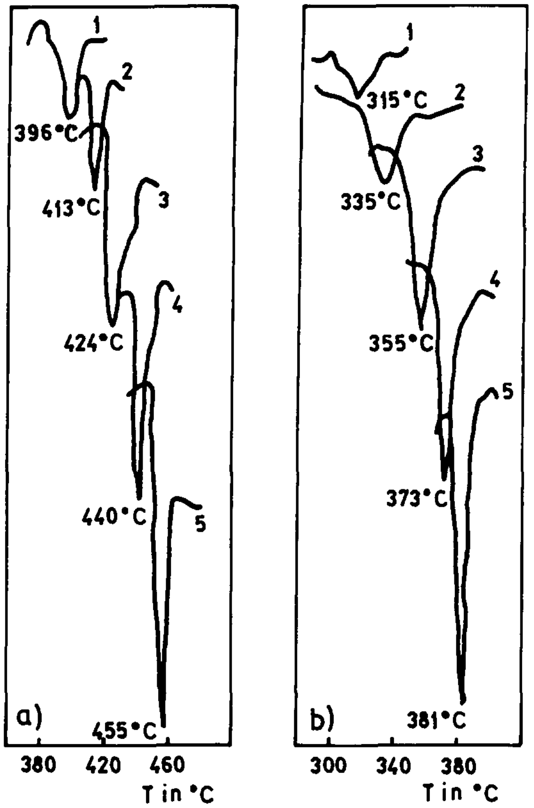

Fig. 1. DTD curves at different heating rates: 1–3 K min^{-1}, 2–5 K min^{-1}, 3–10 K min^{-1}, 4–15 K min^{-1} and 5–20 K min^{-1} for (a) Cu–Zn 15.75 wt%–Al 5.28 wt%; and (b) Cu–Zn 27.60 wt%–Al 3.51 wt%.

The relationships between $\ln\phi/T_m^2$ and $1000/T_m$ (Kissinger method), and between $\ln \phi$ and $1000/T_m$ (Ozawa method) for martensitic and reverse transformations in Cu–Zn 15.75 wt%–Al 5.28 wt% are shown in Fig. 3. and for the Cu–Zn 27.60 wt%–Al 3.51 wt% alloy in Fig. 4.

On the basis of linear relationships obtained, the values for the activation energy are determined. Results for the heating and cooling processes are shown in Table 3.

Considering the results obtained, the following observations may be made:

The transformation in Cu–Zn–Al alloys is characterized by temperature hysteresis, i.e. there is a difference between the temperature of the finish of martensitic transformation into parent phase and the

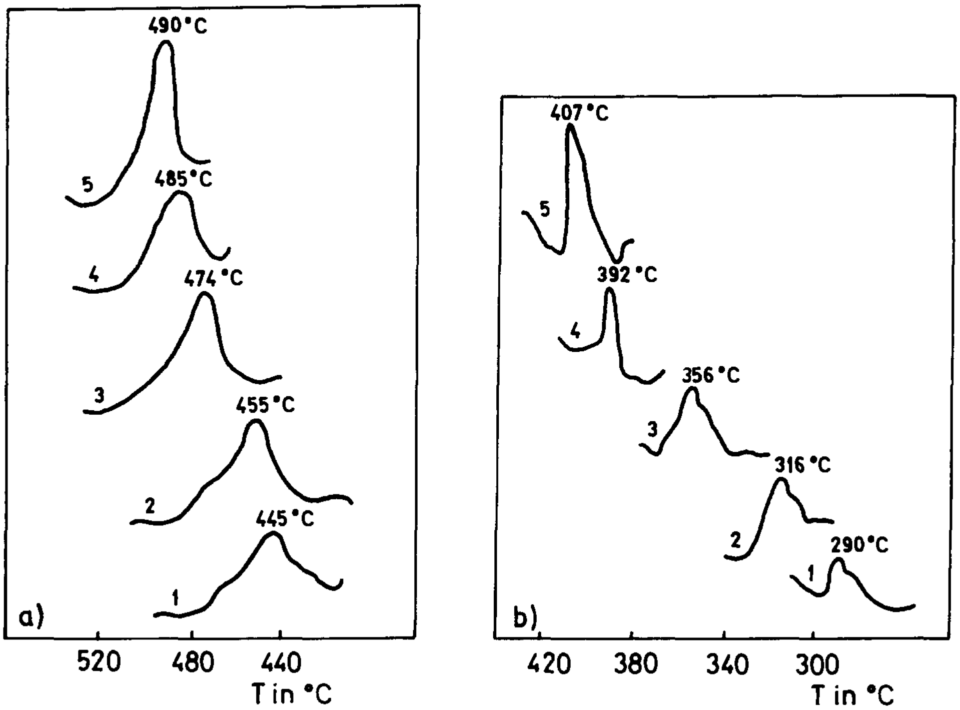

Fig. 2. DTD curves at different cooling rates 1–3 K min^{-1}, 2–5 K min^{-1}, 3–10 K min^{-1}, 4–15 K min^{-1} and 5–20 K min^{-1} for (a) Cu–Zn 15.75 wt%–Al 5.28 wt%; and (b) Cu–Zn 27.60 wt%–Al 3.51 wt%.

temperature of the start of parent phase transformation into martensite (Table 2).

The value of temperature hysteresis of transformation is related to the activation energy for transformation; in Cu–Zn–Al alloys that is a specific quantity of non-chemical free energy, i.e. surface energy and plastic deformation energy.

In essence, the change of energy during transformation in the Cu–Zn–Al ternary system can be described only by means of the parameters that are conditioned by thermal and elastic factors [4], hence this type of phase reaction is called thermoelastic martensitic transformation.

Thermoelastic martensitic transformation during cooling proceeds by continuous growth of martensite crystals and the formation of new crystals. If the cooling is stopped, then the growth of martensite crystal will also stop, but will be renewed with repeated cooling and persists up to the moment when martensite crystals are joined together or with grain boundaries. The transformation of martensite into parent phase during heating proceeds with reverse shifting of the boundary surface of martensite–parent phases, and the martensite crystals decrease and 'transfer' completely into the parent phase.

It should also be pointed that, in this case, the reverse transformation is based on elastic energy accumulated during transformation of the parent phase into martensite.

In this way, the reverse transformation occurs 'prematurely', since accumulated elastic energy promotes the so-called chemical activation energy, provided by heating. The A_s temperature for reverse transformation is accordingly lower than the M_s temperature, therefore we can speak of thermoelastic martensitic transformation of the second order for the investigated alloys, since $A_f > M_s > A_s > M_f$.

It may be observed that temperatures of the start, finish and maximum martensite transformation for the alloy of the first composition are higher than those for an alloy of the second composition. The explanation can be found in the composition of studied samples

Table 2
Start, finish and maximum temperatures of the martensitic and reverse transformation for two different compositions and at different heating and cooling rates

ϕ_{heat}/(K min^{-1})	A_s/°C	A_m ^{a}/°C	A_f/°C
I alloy: Cu–Zn 15.75 wt%–Al 5.28 wt%			
3	346	396	528
5	363	413	542
10	373	424	557
15	390	440	570
20	403	455	583
II alloy: Cu–Zn 27.60 wt%–Al 3.51 wt%			
3	263	315	400
5	280	335	426
10	295	355	452
15	314	373	475
20	331	381	495
ϕ_{cool}/(K min^{-1})	M_s/°C	M_m ^{a}/°C	M_f/°C
I alloy: Cu–Zn 15.75 wt%–Al 5.28 wt%			
3	461	445	330
5	480	455	348
10	515	474	364
15	530	485	376
20	545	490	390
II alloy: Cu–Zn 27.60 wt%–Al 3.51 wt%			
3	341	290	241
5	360	316	259
10	387	356	281
15	415	392	305
20	436	407	315

[a] A_m and M_m correspond to T_m in Kissinger and Ozawa equations.

Table 3
The values of activation energy for two different compounds and at different heating and cooling rates as determined by Kissinger and Ozawa methods

No.	E/(kJ mol^{-1})	
	Kissinger method	Ozawa method
TD		
Heating		
I alloy	124	136
II alloy	82	92
Cooling		
I alloy	171	183
II alloy	40	50

itself; primarily in the differing quantity of added aluminium, since, the larger the content of aluminium the higher the temperatures of martensitic as well as reverse transformations [4]. Also, in Cu–Zn–Al alloys, the region in which β-phase exists with space-centered

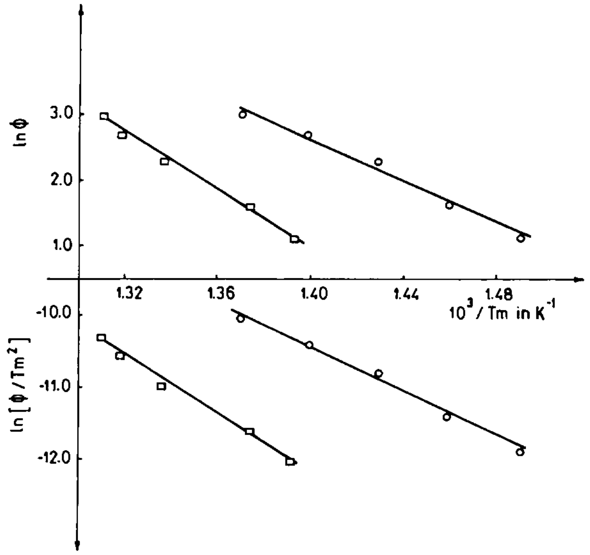

Fig. 3. Relationships between $1000/T_m$ and $\ln[\phi/T_m^2]$ (Kissinger method) and $\ln\phi$ (Ozawa method) for martensitic (□) and reverse (○) transformation in case of Cu–Zn 15.75 wt%–Al 5.28 wt% alloy.

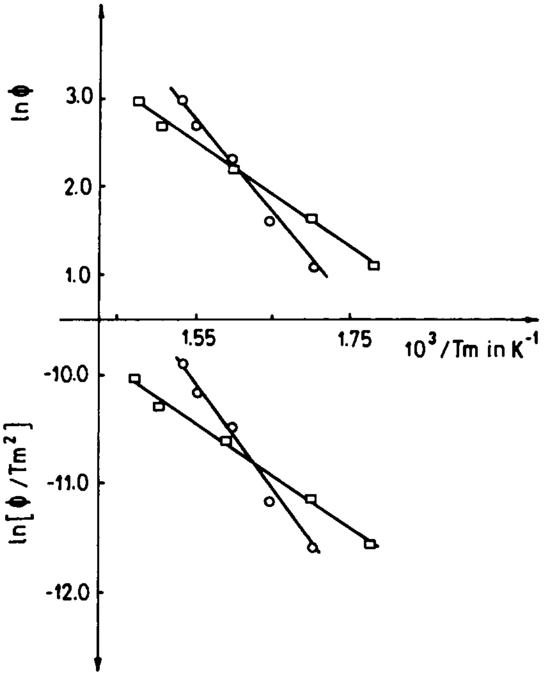

Fig. 4. Relationships between $1000/T_m$ and $\ln[\phi/T_m^2]$ (Kissinger method) and $\ln\phi$ (Ozawa method) for martensitic (□) and reverse (○) transformation in case of Cu–Zn 27.60 wt%–Al 3.51 wt% alloy.

cubic lattice, shifts towards lower concentrations of zinc in addition to aluminium.

Accordingly, an alloy of the first composition, Cu–Zn 15.75 wt%–Al 5.28 wt%, as compared to an alloy of second composition, Cu–Zn 27.60 wt%–Al 3.51 wt%, has higher values for temperatures of the martensitic and reverse transformations, which was proved by DTD method as well.

A summary of results for values of activation energy obtained by DTD method for two different compositions, which are given in Table 3, show a good correlation within the limit of ±5%, which is considered satisfactory for these results.

The activation energy values obtained for two studied compositions are of the same order of magnitude as for Cu–Zn–Al alloys of similar composition, which shows that they are correct. The high values of activation energy over 40 kJ mol^{-1} show that the processes of the martensitic and reverse transformations are surface controlled and that they are in the kinetic region.

Accordingly, the decisive influence on the rate at which shape memory process proceeds is that of temperature, hence the difference in activation energies between the two alloy compositions.

During the heating process, activation energy for an alloy of the first composition is higher than that for an alloy of the second composition, which follows from the alloy composition itself. Since the aluminium content in alloy of the first composition is higher than that for the alloy of the second composition, temperatures of reverse transformation are higher, and with the higher temperature the rate at which the process of reverse transformation proceeds is also higher.

Also, during the cooling process, the activation energy of alloy of the first composition is higher than that for an alloy of the second composition.

However, the activation energy of reverse transformation for an alloy of the first composition is lower than the activation energy of martensitic transformation and vice versa. At the same time, this is reflected in the values of activation energy as well.

As previously pointed out, an increased content of aluminium shifts the region of concentration of β-phase towards lower zinc content so that higher energy is necessary for the initiation of shape memory process during the cooling process and vice versa. At the same time, this is reflected in the values of activation energy as well.

Apart from that, the formation of martensite from parent phase is possible even when Gibbs free energy of martensite is lower than Gibbs free energy of the parent phase. In that, Gibbs free energy is the activation energy for transformation of the parent phase into martensite.

The formation of crystals of martensite not only causes the decrease of Gibbs free energy but also the occurrence of the so-called non-chemical free energy (energy of elastic deformation, surface energy of embryo, energy of plastic deformation connected with deformation in invariant lattice, and energy caused by elastic oscillation of atoms) which acts opposite to Gibbs free energy.

In order to achieve sufficient activation force for the transformation of parent phase into martensite, it is necessary that Gibbs free energy, in absolute value, should be larger than the non-chemical energy, i.e. it is necessary to undercool the alloy to the M_s temperature. Therefore, M_s is the maximum temperature at which martensitic transformation can occur.

On the other hand, activation energy for the transformation of martensite into the parent phase is necessary, i.e. overheating to A_s temperature is necessary.

The reverse transformation is, moreover, based on elastic energy that is accumulated during transformation of the parent phase into martensite. The reverse transformation occurs prematurely, since accumulated elastic energy promotes chemical activation energy provided by heating, in which the A_s temperature for reverse transformation will be lower than the M_s temperature.

Accordingly, for stated reasons, the obtained values for activation energy of the martensitic transformation will be higher for an alloy of the first composition, and lower for an alloy of the second composition, as compared to activation energy for the reverse transformation.

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