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The shape memory effect in systems Cu-based alloys

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Abstract: Till now, the shape memory effect has been found in Cu, Ni, Au, Ag, Nb and Fe-based alloys. Among them, the largest practical usability have Cu and Ni-based alloys but latter have better mechanical properties (higher hardness, better deformability, as well as temperature and corrosive resistance).
Two new chemical compositions of Cu-Zn-Al based alloys were selected in order to analyse their phase transformation and shape memory behaviour. Both chemical compositions of alloys are relative closed to each other and selected in such a manner that their temperatures of martensite transformation M_s would have been above room temperature. The influence of deformation and heat treatment was analysed for both alloys. Temperature of martensite transformation can be measured with different methods. X-ray method and electrical resistivity measurement at elevated temperatures are cited the most frequently in the literature. In the present work, dilatometry (DIL) was used as a new method for a detection of martensite transformation down to –100°C. Transmission electron (TEM) and light microscope with heated table (HT/LM) were used in order to explain and to confirm temperatures of martensite start (M_s), martensite finish (M_f), austenite start (A_s) and austenite finish (A_f) determined by DIL.

Key words: shape memory alloys, martensite transformation

I. INTRODUCTION

A term ″shape memory″ indicates that some types of alloys ″remember″ its own form which have had before deformation and that they have ability to return in it if they are heated above the characteristic critical temperature. Shape memory effect is known since 1932 when it was detected for the first time in Au-Cd-based alloys. Later this effect was observed in many alloying systems. Technically the most important are Cu-Zn-Al, Cu-Zn-Ni and Ni-Ti. Recently, these alloying systems are very attractive. Main reasons for such a big interest are their excellent mechanical properties, especially pseudoelasticity and shape memory effect. In different alloys, martensite transformation can be accompanied, either with the one-way (irreversible), or two-way (reversible) shape memory effect and pseudoelasticity.
Alloys, which possess pseudoelasticity and shape memory effect have reversible martensite transformation with a narrow temperature of hysteresis (5 to 30 °C). By the nature, reversible martensite transformation is thermoelastic. Thermoelasticity is characterised by the quantity of elastic strain energy, which is stored during a transformation of beta (β-) phase into martensite phase. And vice versa, this energy is released during reversal transformation. Thus, martensite transformation can be found in all alloying systems based on Cu, Ag, Au, Ti and Fe, which have a high-temperature β-phase.
Shape memory effect is observed during fast cooling (quenching) of β-phase from high to room temperature. High temperature β-phase has a body centred cubic structure which is formed orderly before onset of martensite transformation. Therefore, formed martensite ″inherits″ long-range order of primary β-phase. Figure 1 shows schematically a martensite transformation course in shape memory alloys.

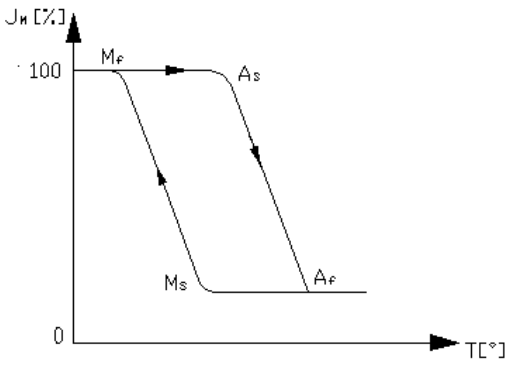

Fig. 1: Schematic presentation of martensite transformation of shape memory alloy [1]

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If alloy with martensite structure is loaded and consecutively elasto-plastically deformed in the structure remains permanent deformation after its unloading. In the case of heating this alloy above temperature of austenite formation (Af) martensite structure and deformation disappear. Original undeformed shape is re-established. The influence of both parameters; e.g.: temperature and deformation on the shape memory alloys is shown in Picture 2. Curve in the upper right corner shows a deformation of alloy with martensite structure at room temperature. Curve in the lower left corner shows an alloy, which is deformed a little above Af temperature when the alloy is in the austenite region.

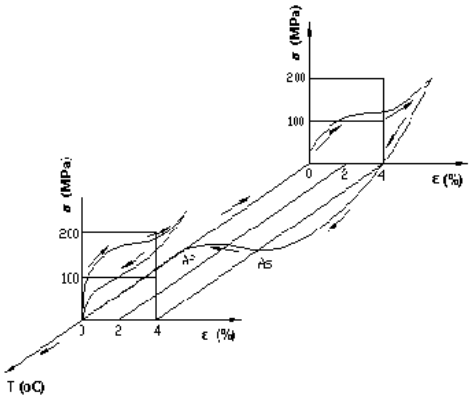

Fig. 2: The behaviour of shape memory alloy at different temperatures and deformations [1].

In many alloying systems, martensite transformations are accompanied either by the reversible (two-way) or irreversible (one-way) shape memory effect and pseudoelasticity.

II. PSEUDOELASTICITY

Term pseudoelasticity means a rubber-like behaviour of material. Material changes its own form reversibly with small stress changes during loading and unloading, respectively.

At stress $\sigma=R_t$ strong deformation occurs. This effect is similar to one-way shape memory effect as it will be shown later. Deformation is returned back ″quasi″ elastically after unloading (Picture 3). This effect is in the connection with stress hysteresis - $\Delta\sigma_h$. Above R_t strong deformation occurs during loading. This deformation is lost and material returns in its original form after unloading already at a little lower stress $\sigma=R_t-\Delta\sigma$ ($A_f < T_3 < M_d$).

Transformation $\beta\rightarrow\alpha$ is induced by the stresses. The selection of crystallographic shear possibilities is in accordance with the direction of main shear stress caused by the main external load, just like in one-way shape memory effect. But a tendency to reversal transformation $\alpha\rightarrow\beta$ is here stronger in comparison with one-way shape memory effect. Alloy behaves pseudoelastically in temperature region from A_f to M_d.

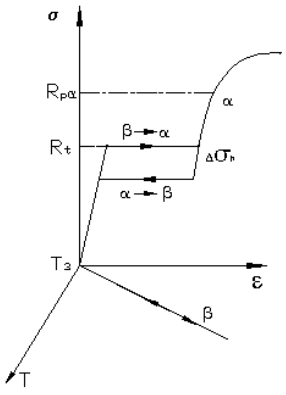

Fig. 3: Pseudoelastic behaviour of certain alloy justabove and below R_t [1].

A. ONE-WAY SHAPE MEMORY EFFECT

Material is pseudo plastically deformed at $R_t<R_p$ if it exhibits one-way shape memory effect. If material is subsequently heated above temperature A_s it starts to change into original form, which it has had in undeformed state (Picture 4).

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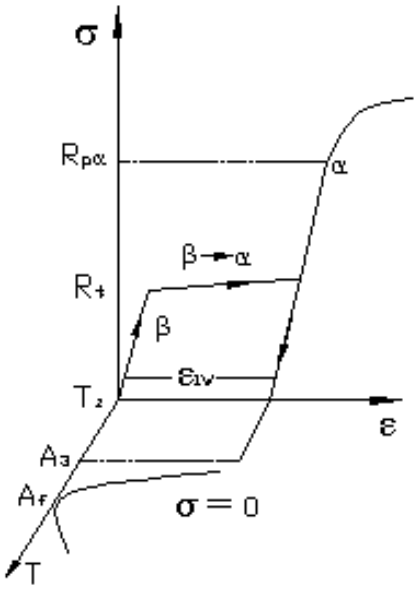

Fig. 4: The behaviour of certain alloy during one-way shape memory effect between A_s and A_f [1].

B. TWO-WAY SHAPE MEMORY EFFECT

Two-way shape memory effect is induced by temperature. Shape is changed if temperature is changed. Maximal obtained deformation is always a little smaller than it is caused by the one-way shape-memory effect. Deformation course is almost discontinuous in a small temperature region with the hysteresis ΔT_h lower than 100 K (Picture 5). During heating, between A_s and A_f strong shape transformation (deformation) occurs but it must be strongly ″in-trained″, previously. Material transforms into its own original shape between M_s and M_f during cooling to room temperature ($OK<T_1<M_f<M_s$). In-training of two-way shape memory effect is possible with a special cyclic deformation and overheating of material, which enables to obtain only one possible martensite variant during transformation of austenite into martensite.

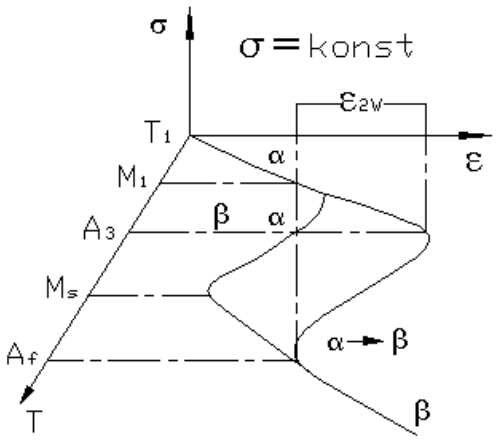

Fig. 5: The behaviour of certain alloy during two-way shape memory effect between A_s and A_f [1].

One-way shape memory effect is characterized by the deformation recovery with heating from A_s to A_f. But, deformation is completely temperature reversible in alloys which possess two-way shape memory effect.

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III. EXPERIMENTAL

For our investigations two alloys from ternary system Cu-Zn-Al were selected and made. Their chemical compositions are given in Table 1. Technically pure Cu, Zn and Al were melted in a graphite pot by middle frequency induction heated furnace. Prepared alloys were then cast into a flat 20 mm thick and 60 mm long metal moulds. Homogenisation annealing of cast ingots was performed at 750 ^{0}C for 24 hours. After that, hot and cold rolling of ingots was carried out. Hot rolling run down to the thickness of 10 mm at initial temperature of 850 ^{0}C. Final 8 mm thick flats were then obtained with cold rolling. Cold rolled samples were then still recrystallization annealed at 650^{0}C for 0.5 hours.

TABLE 1
CHEMICAL COMPOSITIONS OF SELECTED ALLOYS

Alloy designation	Chemical composition (mass %)		
	Cu	Zn	Al
A1	77.5	15.0	7.5
A2	76.3	15.3	8.4

Zn, Al and Cu distributions were determined by the electron probe microanalyser (EPMA). Distributions of individual elements in certain phases were estimated by point and line profile analysis. For both alloys, X-ray phase analysis was performed, also. On the basis of X-ray diffraction patterns, individual phases of alloys were identified by the help of ASTM maps. Dilatometric (DIL) investigations and differential thermal analysis (DTA) were performed by BAHR (Germany) apparatus. Figure 6 shows samples for our investigations turned from cold rolled 8 mm thick plates.

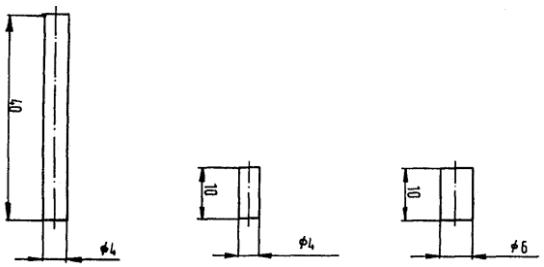

Fig. 6: Samples for DIL and DTA investigations.

Deformation effects formed during turning of samples were eliminated with their annealing at 750 ^{0}C for one hour with slow heating/cooling rate of 2^{0}C/min. Samples were then annealed in high frequency furnace at different temperatures; e.g.: 650, 700, 750, 800, 830 and 1100°C. Samples were at these temperatures isothermally annealed for 30 minutes and then fast cooled to room temperature. Heating rate was 2-5^{0}C/min. (120-300 ^{0}C/h). Temperature was measured by Pt-PtRh 10 thermo-couple. Investigations with HT/LM were carried out with samples of standard dimensions (see Picture 7a). These samples were also turned out from rolled plates and annealed as samples for DIL and DTA investigations.

Investigations were performed with Leitz (Germany) light microscope at magnification 100 ×. Samples were prepared by the standard metallographic procedure before investigation. Heat treatment; quenching series and isothermal annealing were performed in a batch furnace in temperature region form 500 to 750 ^{0}C (in steps by 50 ^{0}C) for 20 minutes. Vickers hardness on the surface of polished samples was also measured (2 to 5 indentations each).

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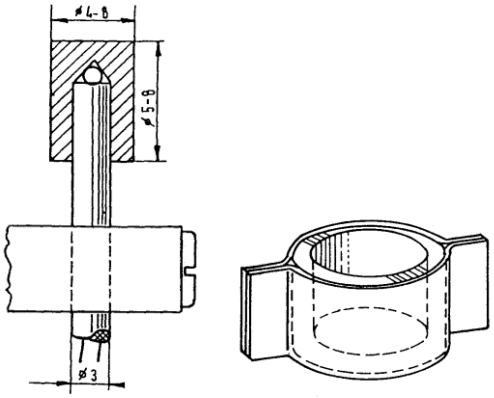
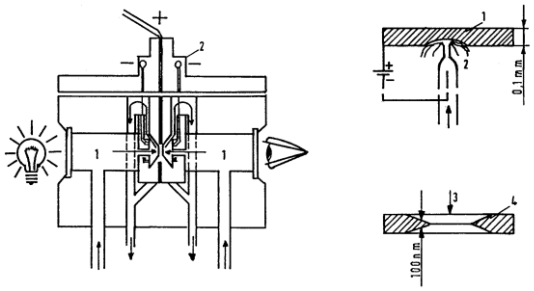


a) **b)**

Fig. 7: a) Samples for investigations with HT/LM and b) heating element

Microstructural changes of etched samples were observed by the LM and TEM. As etching agent water solution of NH_4OH and 3%-H_20_2 was used (20 ml H_20, 20 ml NH_4OH and 20 ml 3%-H_20_2)

First, for TEM investigations, small plates were prepared by diamond saw. From these small plates of thickness of 0.12 to 0.15 µm were then cut out small disks, which were finally thinned by Tenupol apparatus. (Picture 8). Thinning of samples from Cu-Zn-Al alloy was performed with a mixture of CrO_3, saturated H_3PO_4 and 200 ml of H_2O. Thinned samples were then rinsert H_2O and C_2H_5OH. Cleaned samples were kept in paraffin oil preventing surface oxidation. Before microscopy samples were cleaned in petrol-ether.



a) **b)**

Fig. 8: a) scheme of Tenupol apparatus (1- chamber with electrolyte,
2- support with jets for electrolyte dosage and 3- sample)
and b) thinning process of samples
(1 - sample, 2 - jet of electrolyte, 3 - hole, 4 - transmitted region)

IV. RESULTS AND DISCUSSION

As it is evident from Picture 9 (equilibrium microstructure of alloy A1) basic eutectoid arrangement rich in Al and Zn is present. Alpha-phase with significantly smaller content of Zn can also be noticed. X-ray spectra for the same alloy but in the quenched state are given in Picture 10. It can be noticed that the distribution of alloying elements is very uniform.

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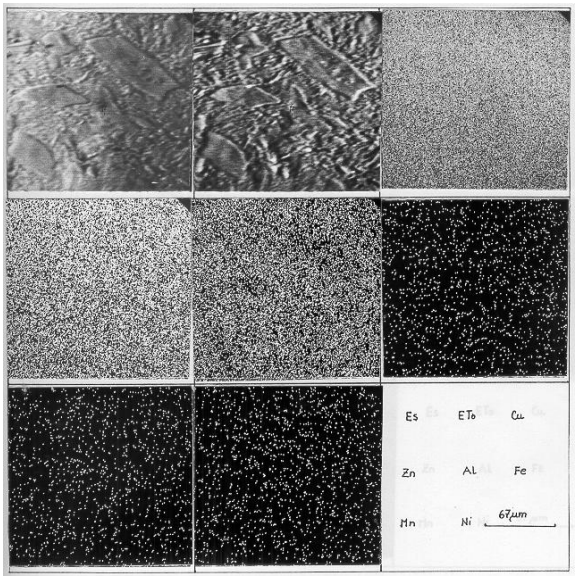

Fig. 9: Characteristic distribution of individual alloying elements and impurities for equilibrium microstructure of alloy A1 determined by EPMA.

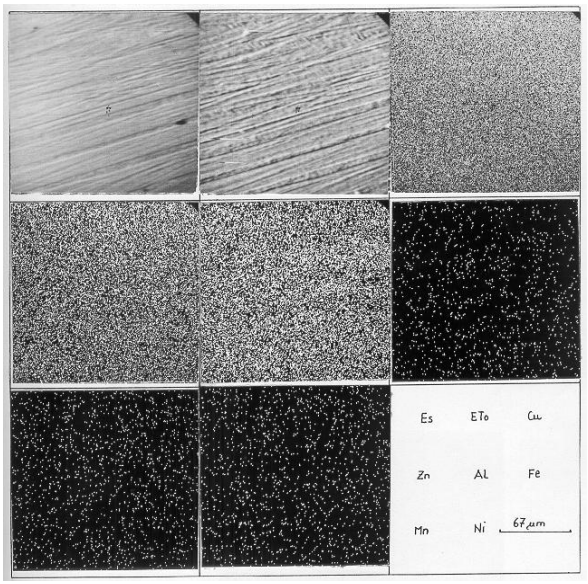

Fig. 10: Characteristic distribution of individual alloying elements and impurities for alloy A1 in the quenched state

V. CONCLUSIONS

Two shape memory alloys from Cu-Zn-Al alloying system were selected and made. Temperature of martensite transformations would have been above room temperature. Formation of this type of alloys is very difficult because of Zn evaporation. Burn out of Zn was approximately 1.5% for A1 and 0.7% for A2. Therefore, alloy A2 has transformation temperature below room temperature.

Annealing and homogenisation at 750 0C diminished microsegregations formed during solidification.

Results obtained by LM are confirmed by EPMA and X-ray phase analysis. The results are in accordance with literature data (6, 8). Some troubles appeared during EPMA because of large absorption of K-α of Al in Cu and Zn. Errors caused by the absorption of X-rays and differences in atomic number between sample and standard were corrected.

Results obtained with point analysis are in accordance with line analysis of microstructural components of both alloys with equilibrium microstructure.

Temperatures of phase transformations were measured by different methods. Investigation with heated table enables a direct determination of a martensite transformation temperature. At this temperature change of sample surface can be noticed because of formation of martensite needles and relief is formed.
Careful observation of sample surface during cooling enabled us to determine M_s temperature where martensite lamellas start to form. During subsequent heating of sample temperature A_f was determined where martensite disappears and high-temperature β-phase appears (starts to form). With this direct evidence of temperature of phase transformations were confirmed temperatures M_s, M_f, A_s and A_f obtained with DIL and DTA (see Table 3).

TABLE 2:
TRANSFORMATION TEMPERATURES OF PREPARED SHAPE MEMORY ALLOYS

Alloy designation	M_s	M_f	A_s	A_f
	°C			
A 1	120	100	132	200
A 2	77	-87	-17	-8

A DIL method was selected because it enables to determine transformation temperatures down to –100 ^{0}C. Prerequisite for the repeatability of results of our investigations is an appropriate heat treatment (homogenisation) of alloys and not too fast heating rate during phase transformation (2-3 ^{0}C/min. max.).

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