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Abstract. The ability of the martensitic transformation of several Cu-Zn-Al alloys produced under industrial circumstances was studied in detail by internal friction and electrical resistance measurements performed mainly above the temperature range of the martensitic transformation. An internal friction peak was found at about 180°C in all alloys. The peak height decreased and the modulus increased during subsequent measuring or after an annealing above the peak temperature. At the same time this heat treatment above 180°C changed also the martensitic transformation ability.

Introduction

The martensitic state which can be produced in some multicomponent copper alloys causes high damping and they can also be used as shape memory alloys [1 - 4] . These properties can allow a wide applicability of the different martensitic alloys in practice. In order to succesfully produce good materials and adjust them to special applications, different elements must be alloyed which can alter the properties of the original alloy. On the other hand, from the point of view of applications, the stability of the martensitic state and/or the shape memory effect is essential. The aim of the present work was to study the temperature stability of three Cu-Zn-Al alloys prepared under industrial conditions by using internal friction (i.f.) with dynamic modulus (d.m.) and electrical resistance (e.r.) measurements.

Experimental procedure

The compositions and the transformation temperatures of the alloys are given in Table 1.

Table 1.

Sample	Composition (wt%) Cu	Zn	Al	M_s (^oC)
1	68.3	27.8	3.5	-7
2.	68.6	26.7	3.4	6
3	70.6	25.6	4.1	116

The ingots of the Cu-Zn-Al (Mn; 0.3 - 0.5 wt%) alloys were prepared by melting the component metals of commercial purity. The ingots were hot- and cold-rolled down to the thickness of about 1 mm. The specimens were annealed at 800^oC for 1 hour and quenched into oil (130^oC, 100^oC) or water (RT, 100^oC) and were aged for different times (600-3600 s). The specimens were stored at room temperature at least 2 hours before the measurements.

Most of the i.f. measurements were carried out in an inverted Kê-pendulum and some specimens were investigated with lateral vibration. The measurements have been made at 1.7x10^{-2}K/s heating rate, the frequency was in the range of 0.4-0.6 Hz and at about 130 Hz. The e.r. was measured by the conventional four probes method.

Results and discussion

The temperature of the martensitic transformation in an alloy depends on the composition and the procedure. The ageing of the Cu-Zn-Al martensite at temperatures below A_s causes the increase of the reverse transformation temperature and so it leads to the stabilization of the martensitic state. Similarly, the ageing at higher temperatures (above M_s) can cause the decrease of the temperature of the martensitic transformation [5].

The vacancy concentration and the degree of order of the β_1 and β_1' phases can be influenced by both the temperature and the time of the ageing process.

In order to study the temperature stability of the alloys, the effect of ageing at different temperatures was investigated. The specimens were aged at different temperatures successively and the e.r.vs.T curves were determined after each treatment (Fig.1). As the temperature of the heat treatments increased, the transformation curves were shifted (by about 30^oC) towards lower temperatures. After a heat treatment at 216^oC for 1 hour no martensitic transformation was detected in the electrical resistance curves (Fig.1). On the basis of detailed study the critical temperature of the disappearing of the martensitic transformation of our alloys was found to be about 180^oC. As it can be seen in Figs.2-4., a new i.f. peak appears in the spectra at about 180^oC, which does not show relaxation character.

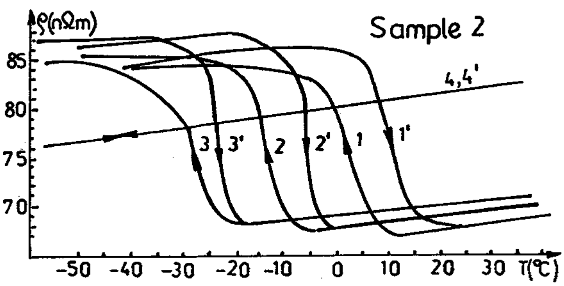


Fig.1. Effect of heat treatments on the e.r. 1,1'- 800^oC/1h Q(RT,w); 2,2'- 1,1' + 138^oC/1h Q(RT,w); 3,3'- 2,2' + 180^oC/1hQ(RT,w); 4,4'- 3,3' + 216^oC/1h Q(RT,w).

The height of this peak depends strongly on the rate of cooling after the annealing at 800^oC. In the spectra of slowly cooled specimens, no martensitic peak appeared and the peak at 180^oC was only small. The peak height of the quenched specimen measured during cooling was considerably lower than the peak measured during the first heating up period. On the other hand, the dynamic modulus (d.m.) of the quenched specimen increased (20-40%) during annealing at 250^oC and during cooling. However, the modulus of the slowly cooled specimen was unchanged (Fig.2).

The change of the d.m. could be increased with a stop-quenching at 100^oC (Fig.3). The increase of the d.m. in this case was about 50%. The i.f. peak at 180^{0}C was also strongly amplitude dependent but the height of the i.f. peak and the modulus changed in the opposite direction. As the degree of the measuring deformation increased the height of the i.f. peak also increased, but the change of the d.m. decreased (Fig.4).

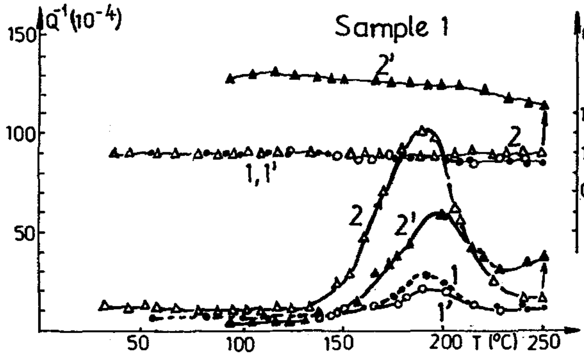
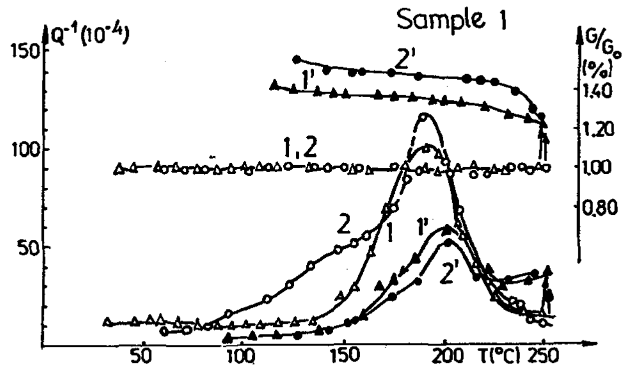


Fig.2. Temperature dependence of the i.f. and d.m. during the first heating and cooling cycle.
1,1'- 800^{0}C/1h + slowly cooled;
2,2'- 800^{0}C/1h + quench (RT,w)

Fig.3. Influence of heat treatment on the i.f. spectra and d.m.
1,1'- 800^{0}C/1h + quench (RT,w);
2,2'- 800^{0}C/1h + 100^{0}C/15 min + quench (RT,w)



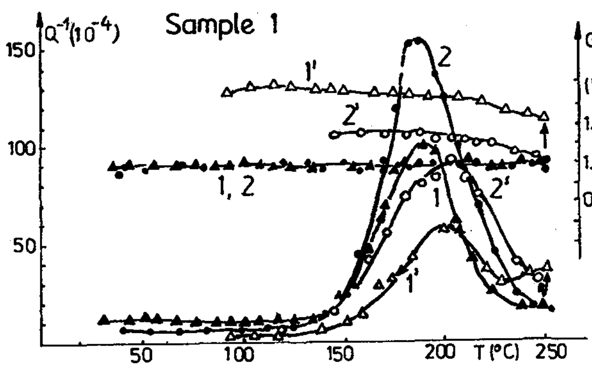


Fig.4. Effect of the measuring amplitude on the i.f. and d.m.
1,1'- small measuring deformation ($\varepsilon = 1.10^{-5}$)
2,2'- large measuring deformation ($\varepsilon = 5.10^{-4}$)

The main results of the measurements which were carried out during successive heating and cooling in the temperature range of 168^{0}C - 240^{0}C (Figs. 5-7):

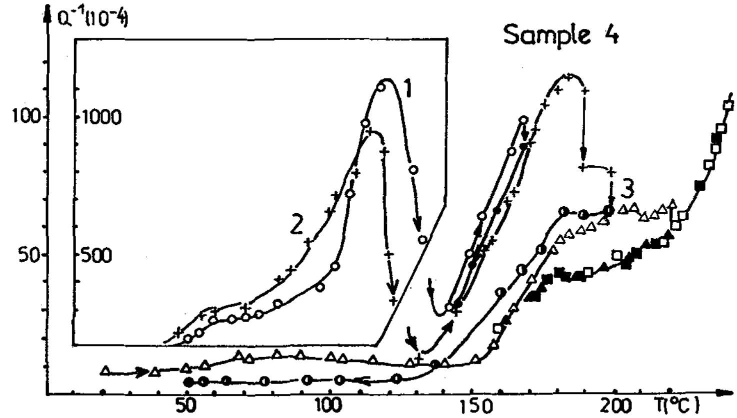
- There is a connection between the martensitic transformation peak and the 180^{0}C peak.
  To the extent that the 180^{0}C peak disappears with annealing, the martensitic peak also decreases and disappears.
- During the decrease of the 180^{0}C peak, the d.m. increases and it can reach 200% of that of the parent phase.

- A relaxation peak can be seen on the background in the range of the 180°C peak after the successive measurements.
- The values of the d.m. measured at constant temperature in the range of the peak produce an increasing curve with time.
- The i.f. curves measured at certain constant temperatures have a maximum between 5 and 20 minutes [6].

From the above results it can be concluded that the change of the internal structure takes place only during the measurements of the quenched specimens. The i.f. spectrum and the modulus of the slowly cooled specimens was unchanged during the heating up to 250°C and the cooling. The appearing and also the disappearing of the 180°C peak and the increasing of the background above the peak temperature are caused by this change of the internal structure of the specimens.

Our opinion is that a precipitation process takes place during the i.f. measurements and during the ageing of the quenched specimens. The instability of the 180°C peak marks the instability of the internal state of the specimen during the measurements, thus the change of the state of the precipitations. After an annealing at 250°C, a stable i.f. spectrum appears with a small peak and with a higher background which remains stable during the measurements between room temperature and 250°C. We can conclude from this that a new stable state develops in the specimens with incoherent particles which causes the increasing of the value of the modulus.

Further investigation is required in order to achieve a precise image about this precipitation process.



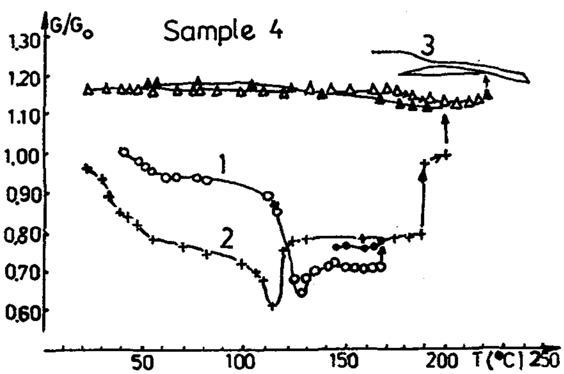


Fig.5a, b. Temperature dependence of the i.f. (a) and d.m. (b) during successive heating and cooling

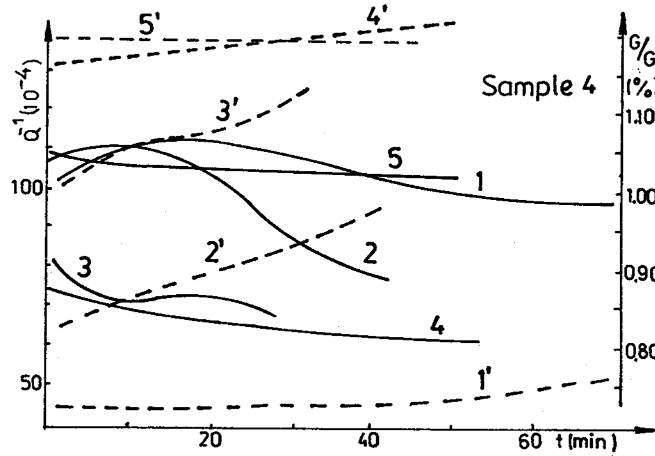


Fig.6. Time dependence of the i.f. (1 - 5) and the d.m. (1'-5') measured at constant temperatures

1,1' - 168°C; 2,2' - 188°C;

3,3' - 198°C; 4,4' - 218°C;

5,5' - 240°C

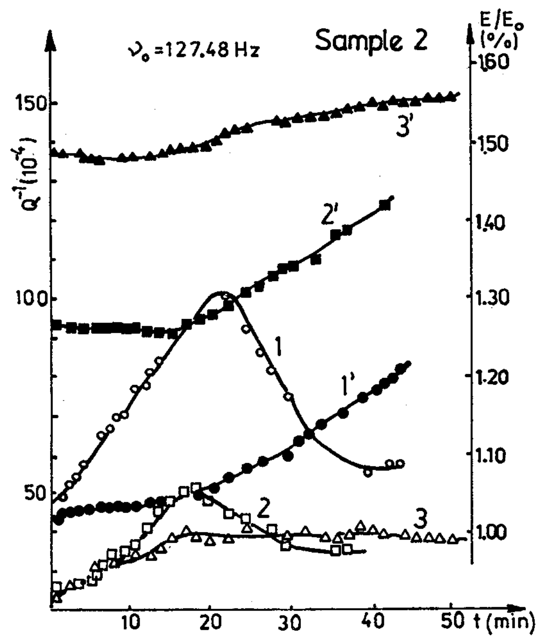


Fig.7. Time dependence of the i.f. (1-3) and the d.m. (1'-3') measured at constant temperature and at high frequency (ν_0= 127.48 Hz)

1,1' - 163°C; 2,2' - 178°C;

3,3' - 192°C

Conclusions

In this work the temperature stability of three Cu-Zn-Al alloys has been studied. We can conclude from the results of our internal friction and modulus measurements that the state of the β_1 phase in our alloys is changed by ageing at about 180°C. The results of the i.f. measurements carried out in the range of the temperature on martensitic transformation indicate that this ageing has an influence of the transformation ability, too. The results of the i.f. and the modulus measurements show that a precipitation process takes place at about 180°C. This process causes the loss of the transformation ability of our alloys.

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