

## Stabilization of Martensite in Cu-Zn-Si Alloy

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### Introduction

The problem of stabilization of martensite ( $\beta'$ ) attracts high interest, especially in Cu-Zn-Al and Cu-Ni-Al alloys. Two main mechanisms of the stabilization process are generally accepted:

a) martensite boundary pinning by the quenched in vacancies or vacancy clusters (1,2), b) modification of the unit cell parameters of martensite, without change of the c parameter, which leads to the more packed structure. This modification is connected with a lowering of the degree of long range order (1,3), what was confirmed also by investigation of the long range order in  $\beta'_1$ '

phase of the Cu-Zn-Al single crystals (4). In the case of fully martensitic sample, after its single-stage quenching the complete stabilization may appear. In the case of the sample containing  $\beta$  and  $\beta'$  phases in the aging temperature, partial stabilization may follow (2,5-7). The partial stabilization leads to the reverse transformation  $\beta' \rightarrow \beta$  in the higher temperature range than  $A_c$  of

the non-stabilized sample (7,8). Diverse opinions are presented in literature concerning the influence of the  $DO_3$  order on the

stabilization of martensite (7,9). In this paper investigation of martensite stabilization in Cu-Zn-Si alloys is presented. The  $\beta$  phase of this alloys exhibits only B2 long range order ( $\beta'_2$ ').

### Experimental

Investigated alloys were melted from a high-purity components in the quartz ampule in an induction furnace. After homogenization and hot-rolling samples were quenched from the high temperature range at the room temperature (RT) water. The chemical composition of the investigated alloys (checked by atomic absorption or polarographic methods) is shown in the Table 1. Samples were aged for about 1 month at RT. They were investigated using following methods: transmission electron microscopy (TEM), differential scanning calorimetry (DSC), electrical resistivity vs. temperature and X-ray diffraction. Continuous heating was used.

In the present paper the results of TEM and DSC methods are presented. Results of other methods were partially presented in (10) and will be published elsewhere.

TEM investigation were performed using Philips EM 301 (100 kV) equipped with a heating holder. Thin foils were prepared by jet

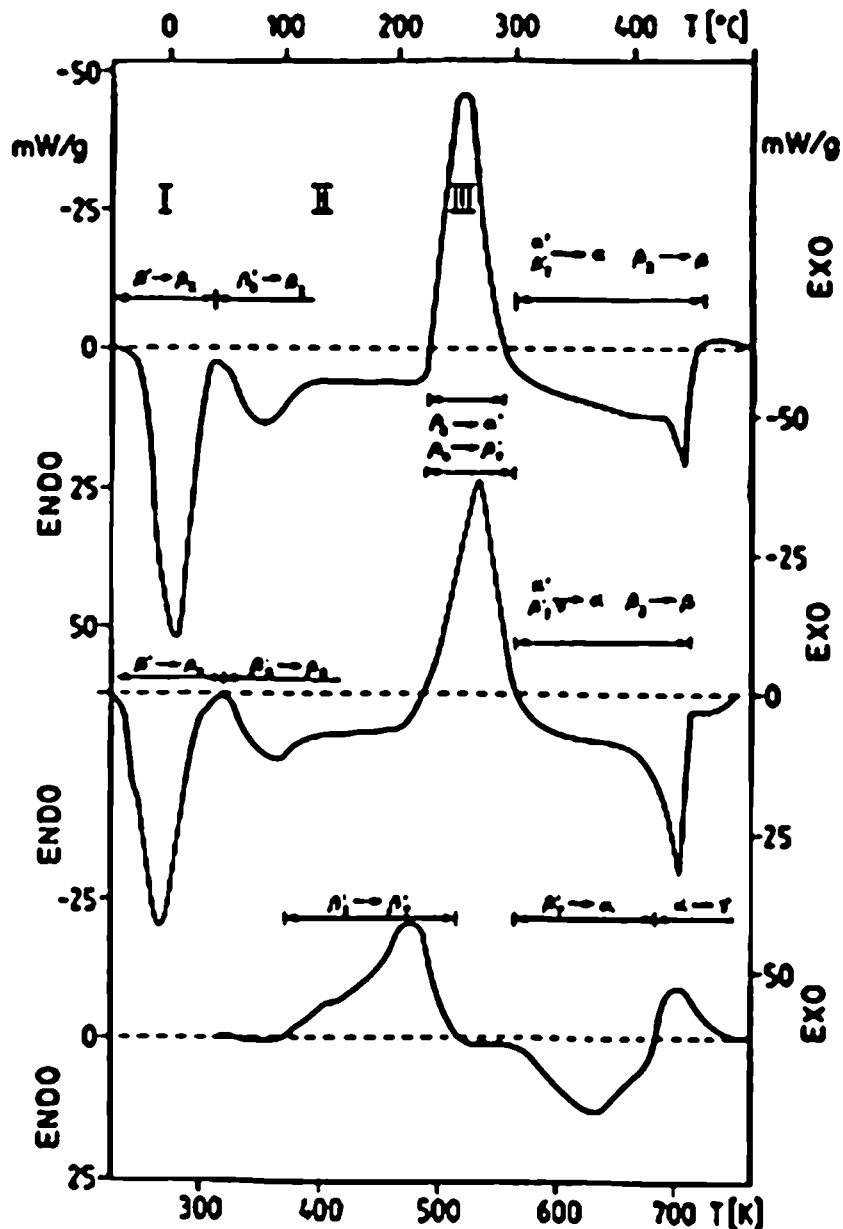
electropolishing in the solution of  $H_3PO_4$  saturated with  $CrO_3$  diluted 1:1 with  $H_3PO_4$  at RT and at the voltage of 10 V. Du Pont Thermoanalyzer Model 990 was used for DSC measurements. Heating rate was 20 K per minute.

| Alloy | Chemical composition (%at.) |      |     | Characteristic temp.(K) |       |
|-------|-----------------------------|------|-----|-------------------------|-------|
|       | Cu                          | Zn   | Si  | $A_s$                   | $A_f$ |
| A     | 64.1                        | 33.6 | 2.3 | 222                     | 318   |
| B     | 64.5                        | 30.9 | 4.7 | 218                     | 314   |
| C     | 66.4                        | 24.7 | 8.9 | >373                    | -     |

Table 1: Chemical composition and reverse transformation characteristic temperatures of the investigated alloys.

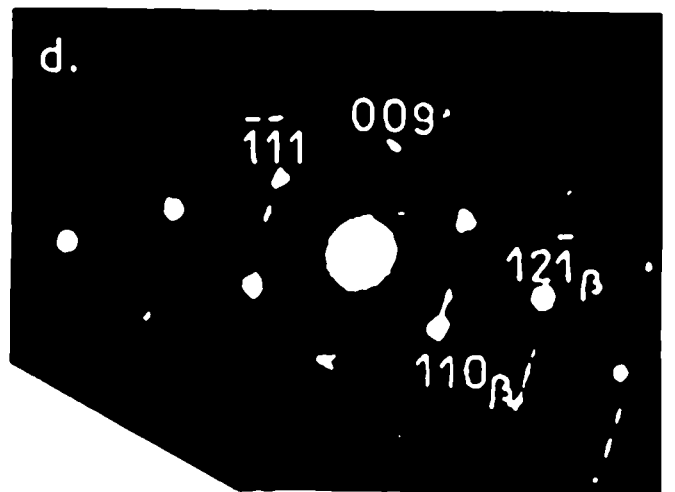
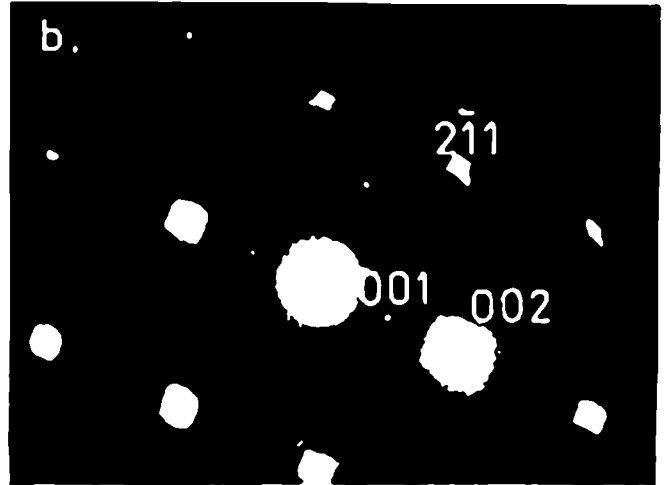
#### Experimental results

In Fig.1 DSC curves are shown. Alloys A and B (in which stabilization process took place) contain at RT a small fraction of the  $\beta_2'$  phase (Tab.1). After stabilization the samples were cooled in liquid nitrogen and then heated at the rate 20 K/min. in the calorimeter. The first thermal effect (I) corresponds to the reverse transformation of thermoelastic martensite, which appeared after cooling of these samples. Fig.2a,b shows that in both samples some fractions of martensitic phase remain in temperature range higher than  $A_f$  ( $\beta_s'$  phase). In the temperature range of a moderate endothermal effect II some plates of the  $\beta_s'$  martensite undergo the reverse transformation  $\beta_s' \rightarrow \beta_2$ , remaining plates in the temperature range of the effect III (exothermal) are stabilized again ( $\beta_s' \rightarrow \beta_T'$ ), Fig.2c,d. The same thermal effect is connected with bainite formation in the  $\beta_2$  phase. Bainite ( $\alpha_B$ ) has the same 9R structure as the martensite  $\beta_T'$  but disordered (Fig.3). The thermal effects in the DSC curves in the higher temperature range than peak III are related to a transformation of phases having 9R structure into  $\alpha$  phase (10,11). Such interpretation of the thermal effects are confirmed by electrical resistivity changes during continuous heating and by X-ray diffraction (10,11). Fig.4 shows a good agreement of the  $dR/dT$  and DSC curves and some results of X-ray diffraction during continuous sample heating for A alloy.

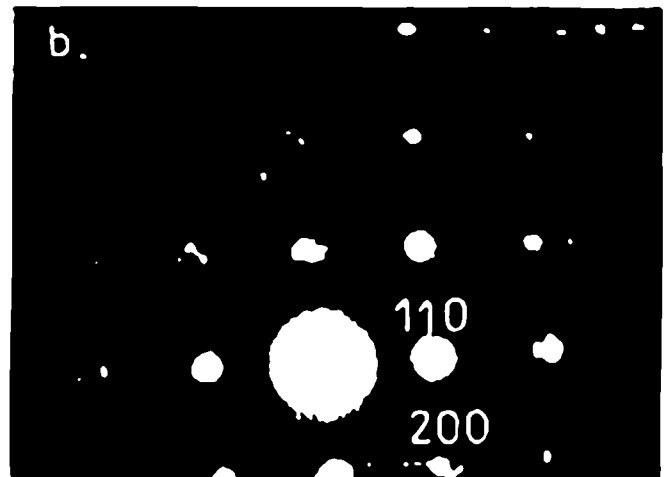
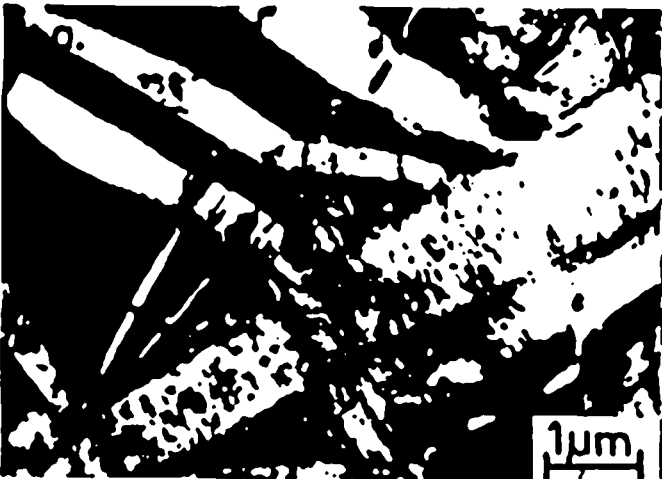


**Fig.1:** DSC curves of investigated Cu-Zn-Si alloys, heating rate 20 K/min.

The DSC curve for alloy C, fully martensitic at RT after stabilization (Fig.5) is different as for alloys A and B, partially martensitic at RT (Fig.1). Endothermal effect connected with reverse martensitic transformation is absent. Exothermal peak (I) cannot correspond to bainitic transformation because in its temperature range the  $\beta_2$  phase does not appear in alloy C. Fig.6 shows electron micrograph and SADP from alloy C in the temperature range higher than thermal effect I. 9R structure remains stable but superlattice spots derived from the matrix phase B2 long range order disappear. The SADP shows lowering of the intensity of the



**Fig.2:** Martensite, stable above  $A_f$  temperature of the A and B alloys, a) alloy A 353 K, b) SADP foil orientation  $[120]_{\beta}$  c) alloy B 380 K, d) SADP foil orientation  $[1\bar{1}0]_{gR'}$ ,  $[\bar{1}11]_{\beta}$ .



**Fig.3:** Alloy A 523 K. a) Bainite plates in  $\beta$  phase, b) SADP, foil orientation  $[001]_{\beta}$

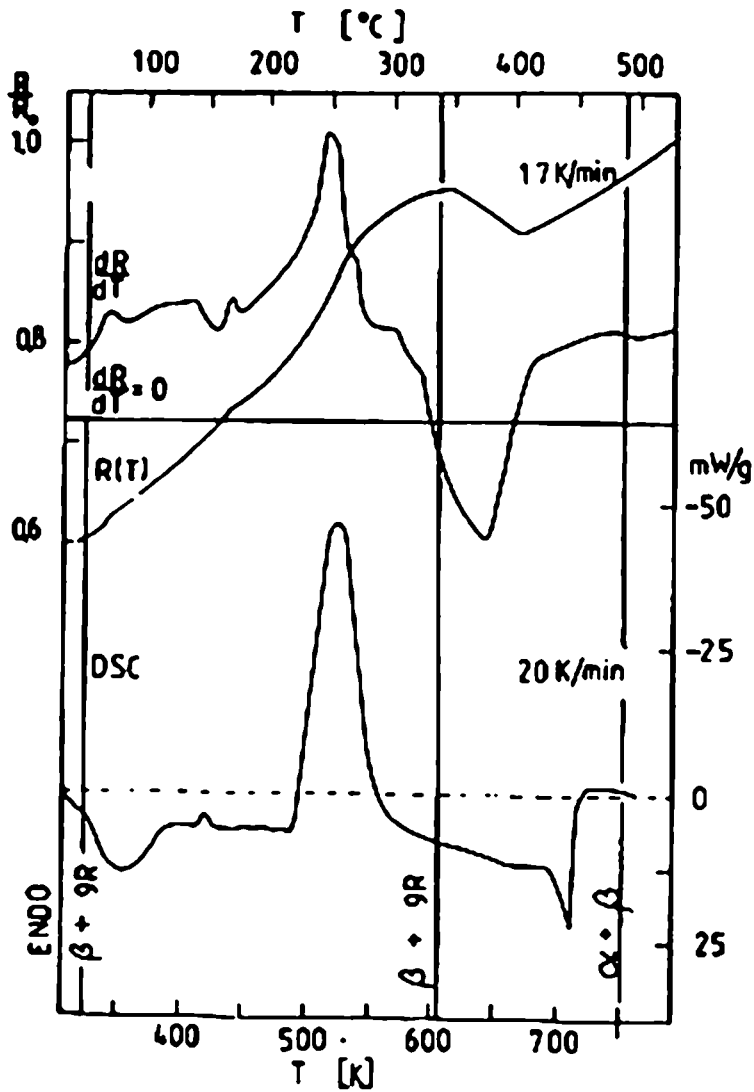


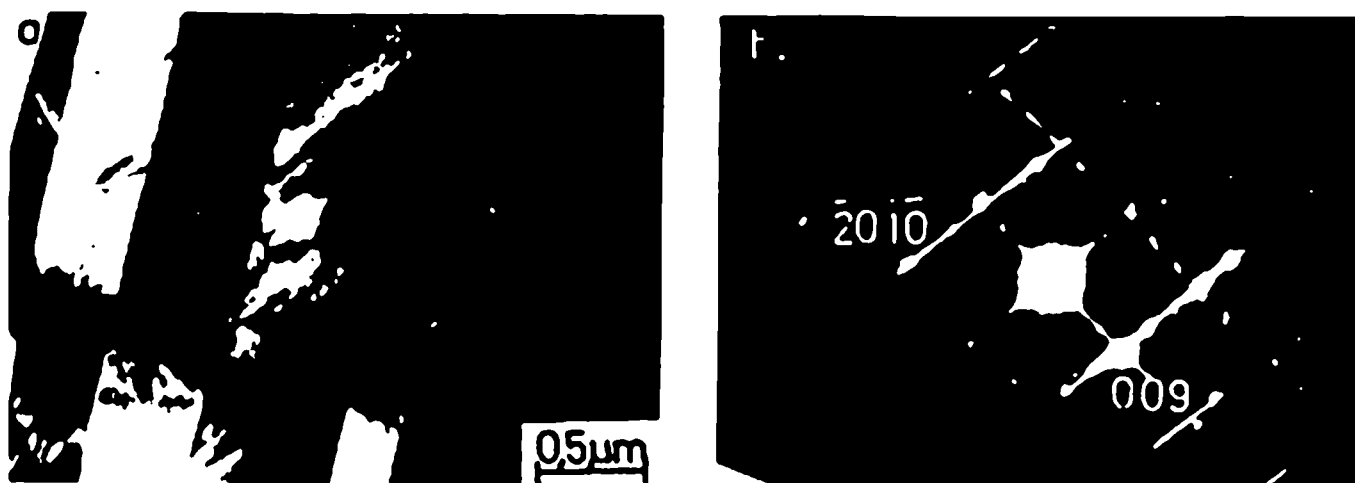
Fig.4: Alloy A. The  $R(T)$ ,  $dR/dT$  and DSC curves. Heating rates: 17 K/min. for  $R(T)$  and 20 K/min. for DSC methods. Results of X-ray phase analysis are shown.



Fig.5: Alloy C, RT. a) Microstructure of  $\beta_s'$  martensite b) SADP, foil orientation  $[0\bar{1}0]_{9R}$ , superlattice spots are indicated by (+).

diffused streaks in  $[001]_{9R}$  direction which suggests lowering of the density of the stacking faults in the martensite structure. X-ray diffraction confirms stability of the  $9R$  structure in the same temperature range and shows the modification of the unit cell parameters which lead to the shift of the  $(204)_{9R}$  line towards the higher  $2\theta$  angles, but without any change of the  $(009)_{9R}$  line position.

Thermal effects in the DSC curves at higher temperature range are connected with transformation of  $\beta_T'$  and  $\alpha_B$  phases possessing  $9R$  structures into  $\alpha$  and  $\gamma$  phases which at the temperature of 755 K are equilibrium ones for alloy C (12).



**Fig.6:** Alloy C, 633 K, a) microstructure of the stable martensite plates  $\beta_T'$  b) SADP, foil orientation  $[0\bar{1}0]_{9R}$

### Discussion

Results described above show that in alloys A and B containing only a small fraction of the  $\beta_2'$  phase at RT and in alloy C completely martensitic, aging at RT resulted in stabilization of martensite. It is probably due to a pinning of martensite plates interfaces by quenched in vacancies or vacancy clusters (1,2). Partially stabilized martensite in alloys A and B at temperatures higher than  $A_f$  undergoes partly reverse transformation into  $\beta_2$  phase and at the same temperature range in which matrix phase undergoes bainitic transformation it is again stabilized. That phase was marked  $\beta_T'$ . Due to a small amount of  $\beta_2'$  phase within alloys A and B its structure changes during second stage of stabilization could not be detected using X-ray diffraction, but

most probably the mechanism is similar as for alloy C. Stabilized martensite structurally does not differ from bainitic phase, because it has 9R disordered structure (13,14). Martensite  $\beta'_s$  in alloy C is fully stable until 350-500 K temperature range in which again stabilization occurs ( $\beta'_s \rightarrow \beta'_T$ ). This process is connected with modification of martensite unit cell parameters, with no change of the c parameter and with disappearing of the long range order. This mechanism was confirmed in the study of Cu-30.4Zn-3.9Si (at.%) alloy (not discussed in this paper), using electrical resistivity vs. temperature and X-ray diffraction methods (10,11). This kind of stabilization mechanism leading to a lowering of the martensite free energy by changes in configurational order in martensite have been observed in Cu-Zn-Al alloys (1,3).

If an alloy is completely martensitic there is no possibility of the diffusion between martensite plates and matrix as in case of A and B alloys containing both  $\beta'_2$  and  $\beta'_s$  phases. Nevertheless there exists possibility of components segregation to interfaces of the  $\beta'_T$  plates or another martensitic (bainitic) structures may appear, 2H for example, in form of thin layers (14) inside the  $\beta'_T$  plates. In the case of A and B alloys because of temperature range and similarity of  $\beta'_T$  and bainite structures, diffusion of the solvent component to the  $\beta'_2$  phase (13,14) may play an important role in the stabilization mechanism in the second stage.

Increasing of 9R structure stability up to temperatures higher than 550 K causes the possibility of direct transformation of most of the stabilized martensite into the fcc  $\alpha$  phase with no participation of the bcc  $\beta$  phase. Similar process was reported for bainite transformation into  $\alpha$  phase in copper based alloys (15).

The electrical resistivity changes with continuous heating allowed to determine influence of Si and Zn content on the start temperature of the second stage of martensite stabilization and bainite formation. Increasing of the Si content or decreasing of Zn content leads to lowering of these temperatures, similarly to influence of these components on the martensite start ( $M_s$ ) temperature in Cu-Zn-Si alloys (16).

### Conclusions

1/ In investigated Cu-Zn-Si alloys 2-stages of the process leading to a stabilization of martensite were found, 1-st stage, after about 1 month aging at RT, 2-nd stage during continuous heating with rates 6-20 K/min.

2/ The 1-st stage is most probably connected with pinning of vacancies mechanism, the 2-nd with modification of the unit cell parameters and disappearing of the long range order within martensite; in alloys possessing both  $\beta_2$  and  $\beta_B$  phases this process may include diffusion, likely as in the case of bainitic reaction.

3/ Thermal effect observed in the DSC curves, connected with the second stage of stabilization process is exothermal and appears in the same temperature range as bainitic reaction in the  $\beta_2$  phase.

4/ Increase of the Si or decrease of the Zn content leads to a lowering of the start temperature of the second stage of the stabilization process.

### References

- (1) Ahlers: Proc. ICOMAT 86, Nara, Japan, (1986) 786
- (2) J.Janssen, J.Van Humbeeck, M.Chandrasekaran, N.Mwabe, L.Delaey  
J.de Phys. C4 43 (1982) C4-715
- (3) L.Delaey, T.Suzuki, J.Van Humbeeck: Scripta Met. 18 (1984) 899
- (4) Y.Hashiguchi, H.Higuchi, J.Matsui, T.Nitanni, H.Tokunoh,  
Y.Ikai: Proc. ICOMAT 86, Nara, Japan, (1986) 832
- (5) J.Van Humbeeck, J.Janssen, Mwaba-Ngoie, L.Delaey: Scripta Met.  
18 (1984) 893
- (6) G.Scarsbrook, J.Cook, W.M.Stobbs: J.de Phys. C4, 43 (1982)  
C4-703
- (7) X.Y.Lu, M.S. Cao: Proc. ICOMAT 86, Nara, Japan, (1986) 856
- (8) M.Mantel, R.Rapaciolli, G.Guenin: Proc. ICOMAT 86, Nara, Japan,  
(1986) 880
- (9) M.de Graef, J.Van Humbeeck, L.Delaey: Proc. ICOMAT 86, Nara,  
Japan, (1986) 850
- (10) J.Dutkiewicz, T.Czeppe, J.Soltys, J.Ryrych: Proc. XIII Conf. on  
Applied Crystallogr., Poland, 1 (1988) 154
- (11) J.Dutkiewicz, T.Czeppe: to be published
- (12) H.Pops: Trans. AIME, 230 (1964) 813
- (13) K.Takezawa, S.Sato: Proc. ICOMAT 86, Nara, Japan, (1986) 625
- (14) M.H.Wu, C.M.Wayman: Proc. ICOMAT 86, Nara, Japan, (1986) 619
- (15) K.Takezawa, H.Watanabe, S.Sato: Proc. Conf. Shape Memory Alloys  
1987, China Acad. Press., 344
- (16) H.Pops: Trans. AIME 236 (1966) 1532