Hyperfine Interactions 28 (1986) 1063-1066 

# MÖSSBAUER STUDY OF THE AGEING EFFECTS ON THE STRUCTURE OF CuZnSn SHAPE MEMORY ALLOY

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Using the $^{119}$Sn Mössbauer spectroscopy the study of ageing effects on the structure of a CuZnSn shape memory alloy was performed.
Two stages of ageing at 200 C were observed.
The first stage is connected with formation of $DO_3$ structure and the second stage with precipitation of $\alpha$ and $\gamma$ phases.

## 1. INTRODUCTION

Special brass alloys are intensively investigated because of their important properties such as shape memory effect.

One of the major tasks in the studies of shape memory alloys is estimation of the correlation between microstructural features of aged parent phase $\beta_1$ and characteristic martensitic transformation temperatures /1,2/.

In this work the Mössbauer study of the ageing effects on the structure of a CuZnSn alloy was performed. The CuZnSn alloys are promising material for applications on account of stability of shape memory effect during cycling and possibility of grain refinement /3/.

## 2. EXPERIMENT

The Cu–33.0 wt.% Zn–5.8 wt.% Sn alloy was prepared from 99.99% pure materials. The ingots were homogenized at 650 C for 4 h and then hot–rolled in ($\alpha+\beta$) state to 0.5 mm thickness. The foil was annealed at 810 C for 15 sec and quenched into room temperature water. The ageing process was carried out at the temperature 200 C for 1,5,10,20,40,100 and 150 min. The characteristic temperatures of the martensitic transformation $M_S$ = –98 C, $M_f$ = –152 C, $A_S$ = –150 C and $A_f$ = –97 C were determined from electrical resistivity measurements.

In order to identify structural changes in aged samples the $^{119}$Sn Mössbauer spectroscopy and the Philips 301 TEM electron microscope were applied.

A standard Mössbauer spectrometer operating in the constant acceleration mode was used. The source was $^{119}$Sn nuclei in $BaSnO_3$ with activity about 5 mCi. For Mössbauer investigations the sample was chemically thinned to 45 $\mu$m thick foil. The Mössbauer spectra were decomposed into Lorentzian lines using a least–square method. The isomer shift (Is) was determined relative to metalic tin absorber.

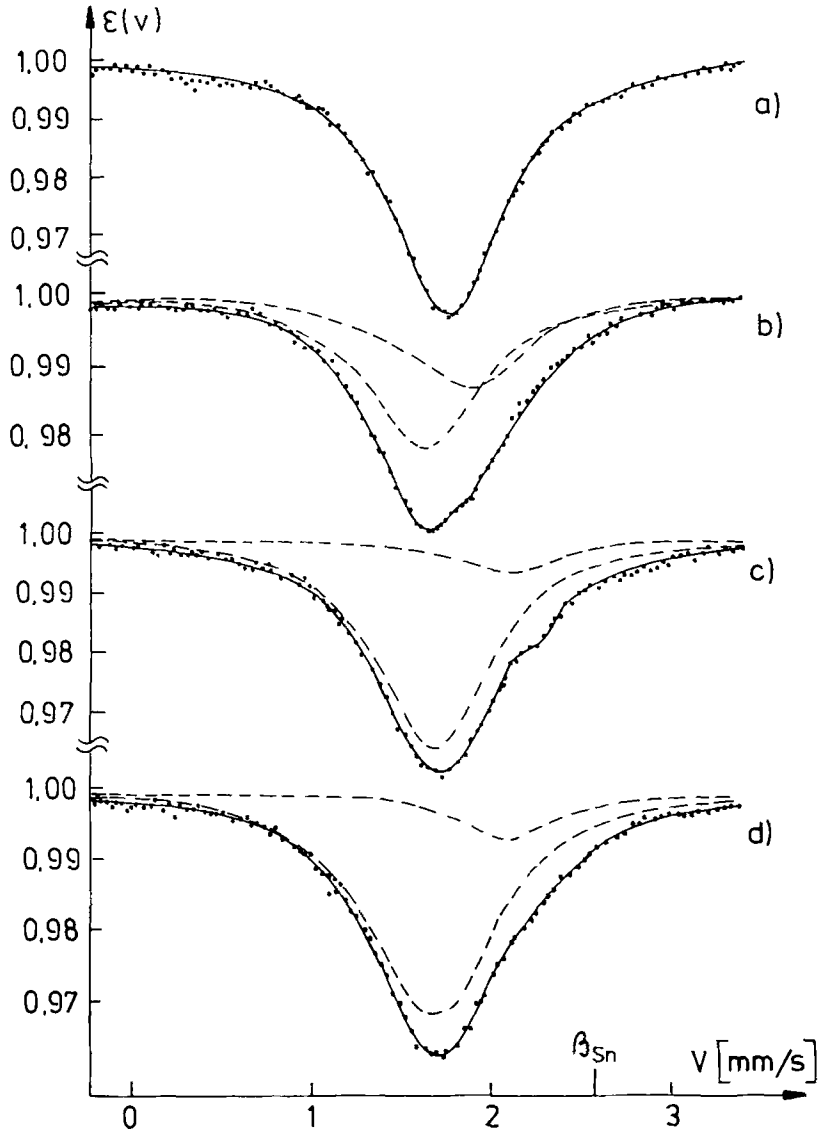


Fig.1. Mössbauer spectra of Cu-33.0 wt.% Zn-5.8 wt.% Sn alloy. a) sample quenched from 810 C b) sample aged at 200 C for 10 min c) sample aged at 200 C for 20 min d) sample aged at 200 C for 150 min.

## 3. RESULTS AND DISCUSSION

The typical $^{119}Sn$ Mössbauer spectra of investigated samples are displayed in Fig. 1. The results of the computer analysis of Mössbauer spectra are collected in Table 1.

Table 1
Parameters of CuZnSn Mössbauer spectra

| Probe no. | Sample | Number of component | Is (mm/s) | Γ (mm/s) | S (%) | Phase |
|---|---|---|---|---|---|---|
| 1 | Hot-rolled | 1 | -0.88 | 0.75 | 89 | α |
| | | 2 | -0.50 | 0.69 | 11 | $\beta_1$ |
| 2 | Quenched from 810 C | 1 | -0.77 | 0.72 | 100 | $\beta_1$ |
| 3 | Aged at 200 C for 1 min. | 1 | -0.79 | 0.76 | 100 | $\beta_1$ |
| 4 | Aged at 200 C for 5 min. | 1 | -0.90 | 0.73 | 82 | $DO_3$ |
| | | 2 | -0.60 | 0.83 | 18 | $\beta_1$ |
| 5 | Aged at 200 C for 10 min. | 1 | -0.94 | 0.69 | 58 | $DO_3$ |
| | | 2 | -0.70 | 0.83 | 42 | $\beta_1$ |
| 6 | Aged at 200 C for 20 min. | 1 | -0.88 | 0.76 | 84 | α |
| | | 2 | -0.49 | 0.88 | 16 | $\beta_1 + \gamma$ |
| 7 | Aged at 200 C for 40 min. | 1 | -0.88 | 0.78 | 90 | α |
| | | 2 | -0.45 | 0.75 | 10 | $\beta_1 + \gamma$ |
| 8 | Aged at 200 C for 100 min. | 1 | -0.90 | 0.79 | 82 | α |
| | | 2 | -0.48 | 0.83 | 18 | $\beta_1 + \gamma$ |
| 9 | Aged at 200 C for 150 min. | 1 | -0.90 | 0.83 | 84 | α |
| | | 2 | -0.38 | 0.77 | 16 | γ |

Is – isomer shift relative to metallic tin absorber
Γ – width of component
S – area under the line

The Mössbauer spectrum of sample quenched from 810 C is a single Lorentzian line. Electron microscope investigations showed that after quenching from 810 C only the B2 superstructure ($\beta_1$ phase) exists in this alloy. The change in the Is value and the broadening of the linewidth compared to those of stoichiometric β phase /4/ are connected with so-called compositional disorder.

The Mössbauer spectra of samples 3 and 4, annealed at 200 C for 5 and 10 min., can be decomposed into two components.

The first component with the value of Is $\leq$-0.9 mm/s can be attributed to Sn atoms having the neighbourhood enriched in Cu atoms in comparison with parent $\beta_1$ phase. Small linewidth suggests that these Sn atoms are substituted regullary and have no other Sn atoms as the nearest neighbours. The electron diffraction has shown that the $DO_3$ superstructure exists in these samples /2/. This makes that the first component is connected with Sn atoms substituted preferentially in one of three sublattices of $DO_3$ structure.

The second component can be attributed to $\beta_1$ phase with smaller long-range order.

The ageing at 200 C for 20 min. causes the next change in the values of parameters of the first and the second component. Is and $\Gamma$ values for the first component are almost the same as the respective ones for hot-rolled sample 1. It suggests that after 20 min. of ageing the process of the precipitation of $\alpha$ phase is started. On the electron micrographs of this sample the plate-like precipitates of the fcc phase ( 3R in Ramsdel notation ) are really observed.

As we can see from Table 1, the linewidth of the second component is anomalously large. This broadening can be explained by assumption that in fact this component is a superposition of the two lines from $\beta_1$ and $\gamma$ phases. This supposition confirms the observation of the change of Is and $\Gamma$ values with the ageing time at 200 C. As we can see the $\Gamma$ value decreases and Is value increases with the time of ageing and reaches the value Is = -0.34 mm/s which is characteristic for $\gamma$ phase /4/.

It is interesting that after 150 min. of ageing the component related to Sn atoms in parent phase was not observed although the electron diffraction results pointed out that there was $\beta_1$ phase present in this sample. It suggests that after long ageing periods Sn atoms are situated mainly in $\alpha$ and $\gamma$ phases.

The observed broadening of the line attributed to $\alpha$ phase with ageing time can be connected with the change of the structure of the bainitic $\alpha$ plates /2/.

## 4. CONCLUSION

The Mössbauer effect and electron microscopy studies of the changes in the structure of Cu-33.0 wt.% Zn-5.8 wt.% Sn alloy after the post-quenching ageing at 200 C leads to the results which may be summarised as follows:

1. The two stages of ageing at 200 C are observed.
2. The first stage is connected with the formation of the $DO_3$ superstructure in the ordered $\beta_1$ parent phase.
3. Results of the Mössbauer effect measurements point out that in the second stage the formation of $\alpha$ phase occurs together with the formation of $\gamma$ phase nuclei. For ageing longer periods only components for $\alpha$ and $\gamma$ phase were observed. Mössbauer effect results suggest also that after longer ageing periods Sn atoms are distributed mainly in $\alpha$ and $\gamma$ phases.

## 5. REFERENCES

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