DSC ANALYSIS OF A CuZnAl TWO WAY SHAPE MEMORY ALLOY DURING AGEING①

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ABSTRACT The degradation behavior of two way shape memory effect in a Cu-20.4Zn-5.6Al (mass fraction, %) alloy by differential scanning calorimetry has been dealt with. Calorimetric technique has been revealed as a powerful way to obtain information concerning the evolution of the trained material. After ageing for several hours at relatively low temperature, the change of martensite from preferred orientation to self-accommodation results in the degradation of TWSME which is recoverable. After ageing at relatively low temperatures (100 ℃, 140 ℃) for longer time or ageing at high temperature (200 ℃), the degradation of TWSME is irrecoverable which results from precipitate.

Key words shape memory alloy two way shape memory effect thermal analysis degradation

1 INTRODUCTION

Two way shape memory effect (TWSME) is well known to be developed in shape memory alloys by thermal-mechanical training a shape memory element under an applied stress[1-4]. TWSME is not a weak effect[3], i.e., it can withstand considerable opposing stresses during cooling through the transformation region[4]. Because the TWSME elements can do work independently, they show a potential application. Thermal stability is an important parameter in applications. During ageing, however, the recoverable strain of TWSME degrades gradually, which limits the life time of the alloys in applications.

Several authors[5-7] have discussed the mechanisms for the degradation of TWSME during ageing. Contardo[6] investigated the temperature degradation of TWSME in CuZnAl and found that TWSME firstly only decreases in amplitude, which should correspond to the trained dislocation annealing, in the second stage the transformation temperatures and the high temperature shape are changed which had been associated with α phase precipitation. Recently, Flores-Zuniga[7] verified the evolution of the trained dislocations during ageing by in-situ TEM observation in CuAlBe alloys and concluded that dislocation gliding during ageing was responsible for the degradation.

In this paper, the similar study was performed for a CuZnAl alloy. However, differential scanning calorimetric (DSC) analysis has been carried out for the degradation of TWSME to investigate this process in more detail.

2 EXPERIMENTAL

A group of specimen strips of 200 mm × 4 mm × 1 mm were prepared by spark-erosion from a Cu-20.4 Zn-5.6Al(%) alloy which was melt in an induction furnace, homogenized at 850 ℃ for 12 h, and rolled into sheet. The material is heat treated at 850 ℃ for 10 min followed by quenching into boiling water, aged at 100 ℃ for 30 min and air cooled to room temperature. The transformation temperatures were measured by DSC to be M_s = 78 ℃, M_f = 40 ℃, A_s = 50 ℃, A_f = 86 ℃. The samples were finally subjected to a so-called combined shape memory effect (SME) and stress induced martensite (SIM)

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training[1]: the samples were bent up around a cylinder mold of 80 mm diameter with a jig in boiling water, followed by being immersed into cold water (some 20 ℃) and putting back to boiling water. This routine is repeated for 30 cycles (4 cycles per minute), a good TWSME can be obtained.

The amount of TWSME was assessed by cycling the samples at unconstrained state between two water baths at 20 ℃ and 100 ℃. Measurements were carried out in the manner indicated in Fig. 1, in which the distances (chord) *AB*, *CD*, *EF*, *GH* were measured at both ends of the sample. *AB* represents the chord in cold state after ageing (L_c), *CD* the chord in its hot state after ageing (L_h), *EF* the length of the sample (L_0), *GH* the deformation imposed during training.

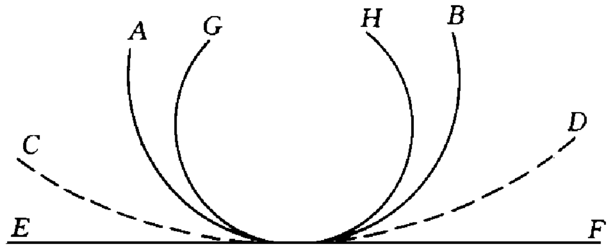

Fig. 1 Schematic representation of shape of specimen

AB —in cold state; *CD* —in hot state;
EF —in original state;
GH —deformation imposed during training

The two way shape memory effect was assessed as:

$$\text{Strength of TWSME } (S_{tw}) = \frac{L_h - L_c}{L_0} \times 100\%$$

If S_{two} represented the strength of TWSME after training but ageing (before ageing) and S_{twh} the strength of TWSME after ageing for *h* hour, the recovery ratio of TWSME after *h* hour of ageing was referred to as:

$$\frac{S_{twh}}{S_{two}} \times 100\%$$

Calorimetric measurement was done in a Perkin-Elmer DSC-7 differential scanning calorimeter to complement the information obtained from degradation measurement. The $\beta_1 - \beta'_1$ forward transformation on cooling was accompanied by exothermic peak, whereas the $\beta_1 - \beta'_1$ reverse transformation on heating gave rise to endothermic peak. The transformation temperatures were determined as the points of intersection of the baseline and the tangent to the peak curve at the inflection point. The total area of the peak corresponds to the transformation heat and was determined directly by the firm software.

3 RESULTS AND DISCUSSION

Fig. 2 shows the evolution of recovery ratio of TWSME as a function of ageing temperatures and ageing time. As shown, the recovery ratio of TWSME decreases during ageing and the higher the ageing temperature is, the sharper the decrease of TWSME will be followed.

Table 1 is a list of comparative data of latent heat of martensitic transformation for different ageing temperature and time. The calculation is carried out by the formula:

$$\Delta G^{P\to M} = \Delta H^{P\to M} - T\Delta S^{P\to M}$$

Table 1 Thermodynamic data of a CuZnAl shape memory alloy during ageing

Ageing mode	M_s /K	A_f /K	T_0 /K	$\Delta H^{M\to P}$ /J·g^{-1}	$\Delta H^{P\to M}$ /J·g^{-1}	$\Delta S^{M\to P}$ /J·g^{-1}·K^{-1}	$\Delta S^{P\to M}$ /J·g^{-1}·K^{-1}
as-trained	348	362	355.0	4.54	-4.21	0.0128	-0.0119
100 ℃, 2 h	346	365	355.5	5.06	-4.69	0.0142	-0.0132
100 ℃, 10 h	344	366	355.0	5.45	-5.43	0.0154	-0.0153
140 ℃, 2 h	345	363	354.0	5.14	-4.81	0.0145	-0.0136
140 ℃, 10 h	343	364	355.5	5.37	-5.30	0.0152	-0.0150
200 ℃, 2 h	340	363	351.5	3.67	-3.10	0.0104	-0.0088

The equilibrium temperature T_0 in the phase transformation is estimated according to $T_0 = 0.5(M_s + A_f)$[14]. When $T = T_0$, the following formula exists:

$$\Delta S^{P\to M} = \Delta H^{P\to M} / T_0$$

where $\Delta G^{P\to M}$ = free energy difference between martensite and parent phase

$\Delta H^{P\to M}$ = enthalpy change of the sample in martensitic transformation

$\Delta S^{P\to M}$ = entropy change of the sample in martensitic transformation

From these results in Table 1, it is known that the evolution of latent heat bears relationship with ageing temperatures and time. Ageing at relatively lower temperatures (100 ℃ and 140 ℃) in parent phase results in an increase in latent heat. On the contrary, a higher temperature (200 ℃) ageing makes the latent heat decrease.

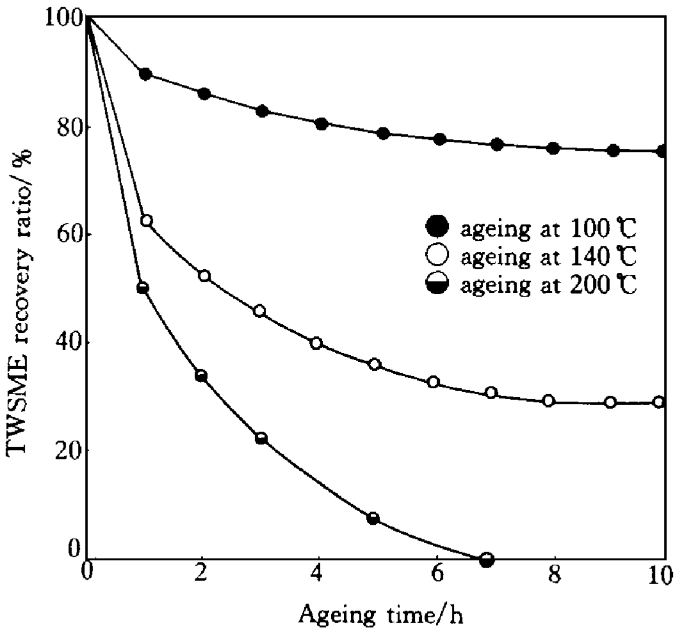

Fig. 2 Two way shape memory effect (TWSME) as a function of ageing time and ageing temperature

It is well known that the martensite variants in one way shape memory alloy mutually show good self-accommodation, so minimizing the strain energy. After thermo-mechanical training, the arrays of introduced dislocations would remain in the parent phase. During the martensite nucleation and growth, the stress fields of the dislocations assist the preferential growth of martensite variants, thus causing TWSME. However, these preferably oriented martensite variants show lesser degree of self-accommodation[9], and excess elastic strain energy is stored in the sample. During cooling, the phase transformation is an exothermic process, some of the latent heat liberated is dissipated as the stored elastic strain energy due to the lesser degree of self-accommodation of the trained martensite, i.e., $\Delta H^{P\to M}$(one way) > $\Delta H^{P\to M}$(two way). Reversely, during heating, the phase transformation is an endothermic process. The stored elastic strain energy in the trained sample will be released when martensite converts back to the parent phase. Therefore, the heat needed for the transformation is less when compared with the untrained sample, i.e., $\Delta H^{M\to P}$(one way) > $\Delta H^{M\to P}$(two way)[10]. When ageing at 100 ℃ and 140 ℃ respectively, the latent heat of martensitic transformation rises, meaning that the evolution of preferably oriented variants into other variants or even into variants of other self-accommodation groups.

Just stated above, the TWSME has been attributed to the residual stress fields of dislocation arrays developed during training[2, 11], the most favorable variants are those whose basal plane coincide with the glide plane of the dislocations, where the dislocations have the lowest energy, i.e., training results in a decrease of the free energy of the trained variants as compared with the free energy of the non-trained variants[13]. Recently, the moving of dislocation arrays resulting from ageing has been proved by in-situ TEM observations[7]. The large evolution of dislocation configurations must involve large change in the local internal stress state of the samples. Thus the number of preferably oriented martensite variants decreases, which are related to the stress field of the introduced dislocations. Some variants, which before ageing are thermodynamically more favored than other crystallographically equivalent variants, are now thermodynamically equivalent to other non-trained variants. In other words, after ageing the amount of non-trained variants is relatively increased. So the degree of the self-accommodation is enhanced, and the TWSME is weakened.

After ageing at 100 ℃ and 140 ℃ for 10 h, the recovery ratio of TWSME becomes 70% and 31%, respectively. A new training is carried out for the degraded samples with the method given in the experiment. Consequently, the recovery ratio of TWSME becomes 98% from 70% for ageing at 100 ℃, and 95% from 31% for ageing at 140 ℃, respectively. It affirms the above statement again that during ageing the morphology of martensite changes from preferred orientation to self accommodation, and after training, the favored variants are obtained again.

In Table 1, $\Delta H_{140 ℃, 2h} > \Delta H_{100 ℃, 2h}$ is understandable, because the moving of dislocations is a thermally activated process. The higher the temperature is, the more rapidly the dislocations move, and the better the martensite variants accommodate themselves, and the more serious the degradation of TWSME gets. But for longer ageing time, $\Delta H_{140 ℃, 10h} < \Delta H_{100 ℃, 10h}$ is a result of precipitate (α phase)[6]. When precipitate forms in samples, the amount of thermoelastic martensite decreases.

Similar to this case, when ageing at 200 ℃, the latent heat of martensitic transformation decreases drastically, which is directly connected with the α precipitate. The degradation of TWSME in an alloy relating to the precipitate is irrecoverable.

4 CONCLUSIONS

The ageing behavior of TWSME with composition of Cu-20. 4Zn-5. 6Al(%) was studied by differential scanning calorimetry. Calorimetric technique has been revealed as a powerful way to obtain information concerning the evolution of the trained material. Ageing for several hours at relatively low temperatures (100 ℃, 140 ℃), the degradation of TWSME is recoverable resulting from the morphology change from preferred orientation of martensite to self accommodation. Ageing for longer time or at higher temperature (200 ℃), the degradation of TWSME is irrecoverable which results from precipitate.

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