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EFFECT OF Mn CONTENT ON KINETIC PARAMETER DURING PHASE TRANSFORMATION IN CuZnAlMnNi SHAPE MEMORY ALLOYS①

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ABSTRACT The effect of Mn content on kinetic parameter during phase transformation in CuZnAlMnNi shape memory alloys at different rising or falling rates of temperature was studied by using the technology of differential scanning calorimetry. It indicated that there is no linear relationship between the variation of apparent activation energy and frequency factor, and the Mn content during phase transformation.

Key words Mn content CuZnAlMnNi shape memory alloy phase transformation kinetic parameter

1 INTRODUCTION

More and more attention is being paid to Cu-based shape memory alloy with the development of advanced technology. There have been a lot of studies about the shape memory effect and the stabilization mechanism of martensite in the alloys[1, 2], but there is no report about the effect of Mn content on kinetic parameter during phase transformation in CuZnAlMnNi shape memory alloys. This paper studies the effect by changing Mn content and using the technology of differential scanning calorimetry.

The apparent activation energy for the memory actuator, which needs high precision of temperature controlling, is not too big, or it will affect the precision. So the study has direct instructing significance for optimizing the design of the composition.

In addition, it may provide a way of DSC for studying the phase transformation kinetics of shape memory alloy. This is the purpose and meaning of the paper.

2 EXPERIMENTAL

2.1 Sample manufacturing

According to the designed proportion, Cu, Zn, Al, Mn and Ni were compounded and put into a WGG- 0.25 type of induct stove, then the ingot of 50 mm in diameter was obtained after being melted. The ingot was rolled into the slice of 1 mm in thickness at 800 ℃ after diffusion-annealing at 850 ℃, 12 h. After solution-treatment at 840 ℃, 20 min, the sample was quenched into water of 100 ℃ and kept 30 min, then it was cooled to room temperature in the air. The alloy after the above treatment belongs to polycrystal. The tested composition for the three alloys is shown in Table 1.

2.2 DSC experimental

The two surfaces of the tested sample were polished to make it contact enough with the sample cell. The mass of sample $1^{\#}$, $2^{\#}$ and $3^{\#}$ was 72.5, 76.8 and 77.5 mg respectively. The mouth of sample cell was sealed by a SCC- 30

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type of sealer when the sample was put into it. The DCS-41 differential scanning calorimeter made in Shimadza, Japan, was used, whose precision of heat energy is 0.5%, and the experimental parameters are 40 mL/min for flow speed of nitrogen atmosphere, 10 mJ/s for AMP range, $-10\sim140$ ℃ for scanning temperature range, liquid nitrogen for cooling medium, 2, 5, 10, 15, and -2, -5, -10, -15 ℃/min for temperature rising and falling rates. The processes of temperature rising and falling can transfer automatically. The sample doesn't change its shape and the martensite doesn't stabilize during the experimental process.

Table 1 Compositions of the samples(%)

Sample No.	Cu	Zn	Al	Mn	Ni
1	71.09	23.9	4.41	0.43	0.17
2	71.23	23.9	4.47	0.23	0.17
3	71.75	23.6	4.35	0.17	0.13

3 RESULTS AND DISCUSSION

3.1 Variation of apparent activation energy during phase transformation

The tested peak temperature T_p for different rising and falling rates of temperature in each sample is shown in Table 2. There are 6 straight lines obtained from the relationship of lg Φ to $1/T_p$ and shown in Fig. 1. The apparent activation energy for each sample during positive and adverse martensite transformation from the line slope and the equation $\Delta E \approx -2.19R\cdot \mathrm{d}\lg\Phi/\mathrm{d}(1/T_p)$[3] (where ΔE and R are apparent activation energy during phase transformation and gas constant, $R = 8.314$ J/mol·K) can be gained[4] as shown in Table 3. For the same sample, T_p only improves slightly with the increasing of temperature rising rate[5], but for the different samples, the variation of T_p connects with that of the compositions when the rising and falling rates of temperature are determined. The relationship between the starting transformation temperature of martensite and the content of Zn and Al is: $M_s = 1890 - 51\%\,\mathrm{Zn} - 134.5\%\,\mathrm{Al}$[6]. It can be found from the equation that Ms decreases with the increasing of Zn and Al, and T_p inevitably decreases with Ms. There is the same law for Mn to T_p from Table 1 and 2. Because of the variation of T_p, the line slope for lg Φ to $1/T_p$ changes evidently (asin Fig. 1), and this leads to the alteration of apparent activation energy during phase transformation (as in Table 3). It can be seen from Table 1 and Table 3 that during the transformation from martensite to mother phase, when Mn increases from 0.23% to 0.43%, the apparent activation energy doesn't fall continually but increases extremely. The three points are not on a line and exist more differences. So when Mn content varies at the range of 0.17% ~ 0.43%, the energy is not the linear function of Mn content,

Fig. 1 Relationship between lg Φ and $1/T_p$

1, 2, 3 and 1′, 2′, 3′ —processes of temperature rising and falling for sample 1#, 2#, 3#

Table 2 T_p for different rising and falling rates of temperature(K)

Rate/℃·min⁻¹	2	5	10	15	−2	−5	−10	−15
Sample 1	300.65	301.65	302.55	303.45	292.15	290.65	289.45	287.65
Sample 2	317.15	322.25	326.05	326.85	312.15	311.35	310.05	309.15
Sample 3	343.05	344.15	346.85	348.05	335.85	334.85	333.25	331.35

that is, the energy neither decreases nor increases all the time with the increasing of Mn content. Meanwhile, during the transformation from mother phase to martensite, the energy has the same law too.

Table 3 ΔE during positive and adverse phase transformation

Sample No.	$\Delta E_{M\to P}$ / kJ·mol^{-1}	$\Delta E_{P\to M}$ / kJ·mol^{-1}
1	390.92	−208.11
2	166.42	−360.56
3	253.45	−192.09

3.2 Effect on frequency factor

Martensite transformation in Cu-based shape memory alloys is first-order ($n = 1$) transformation[7]. According to the Mass-action Law and Arrhenius equation, the kinetic equation of martensite transformation can be written as follows

$$\frac{d\alpha}{dt} = A \cdot \exp(-\Delta E/RT)\cdot(1-\alpha) \quad (1)$$

Where α and A are transformation amount of martensite and frequency factor.

Table 4 Kinetic parameters at 10 ℃/min

Sample No.	Φ / ℃·min^{-1}	H_T / mJ	$H_T - H$ / mJ	dH/dt / mJ·s^{-1}
1	10	−201.62	−112.0	−3.1
	−10	172.1	100.6	1.75
2	10	−274.5	−155.01	−4.08
	−10	267.92	162.9	2.9
3	10	−276.81	−144.96	−4.7
	−10	262.98	153.8	3.0

when $\alpha = H/H_T$ (where H and H_T are phase transformation enthalpy at T_p and the total enthalpy during phase transformation), the equation $d\alpha/dt = 1/H_T \cdot dH/dt$ can be obtained. From these, the following equation can be drawn

$$A = \frac{1}{H_T - H}\cdot\frac{dH}{dt}\cdot\exp(\Delta E/RT) \quad (2)$$

Putting T_p at 10 ℃/min as shown in Table 2 and the values from Table 3 and Table 4 into Eqn. (2), the calculated frequency factors are as shown in Table 5.

Table 5 A values during positive and adverse phase transformation

Sample No.	$A_{M\to P}$ / s^{-1}	$A_{P\to M}$ / s^{-1}
1	8.63×10^{65}	4.8×10^{-40}
2	1.21×10^{25}	3.19×10^{-63}
3	4.8×10^{36}	1.52×10^{-32}

It can be found from Table 5 that there is approximately the same law for the effect of Mn content on frequency factor and on apparent activation energy.

4 CONCLUSIONS

(1) The apparent activation energy during positive and adverse martensitic transformation is not the linear function of Mn content in CuZnAlMnNi shape memory alloy after solution-treatment, that is, when the Mn content is at the range of 0.17% ~ 0.43%, the energy doesn't always decrease or increase with the increase of Mn content.

(2) The frequency factor is not the linear function of Mn content at the above range.

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