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Gamma irradiation-induced evolution of the transformation temperatures and thermodynamic parameters in a CuZnAl shape memory alloy

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Abstract

The effect of the gamma irradiation on transformation temperatures and thermodynamic parameters of the CuZnAl shape memory alloy irradiated with different doses has been investigated. The evolution of transformation temperatures was studied by differential scanning calorimetry (DSC). It was found that the gamma irradiation have a prominent effect on the transformation parameters of the CuZnAl shape memory alloy. The temperature M_f, A_s and A_f shift by the different amount as M_s. It is found that the elastic strain energy and Gibbs free energy decreased by about 27 and 47% with gamma irradiation applied, respectively. The nominal displacement per atom (dpa) level was estimated as $\sim 10^{-5}$.

Keywords: Shape memory; Gibbs free energy; Elastic strain energy

1. Introduction

CuZnAl alloys exhibit shape memory effect within a certain range of composition which have the disordered β bcc phase stable at high temperature and two successive ordering transitions during cooling. The first one occurs at about 800 K, resulting in the B2 structure, which involves the ordering of the nearest neighbors. At a low temperature, which depends on the alloy composition, the second neighbor order, resulting in D03 (or L21) type structure, and then transforms into 9R (or 6M) or 18R (6M) martensite with or without further cooling, depending on alloy composition [1,2]. The effect of gamma irradiation on shape memory alloys (SMAs) is important for their practical applications. It is also a method for the study of condensed matter, which is related to change in the properties by the introduction of point defects. The effects of neutron, proton and electron irradiation on TiNi, TiNiCu, CuZnAl and CuAlNi shape memory alloys have been extensively investigated [3–12]. The results indicated that the irradiation has a very strong influence on the martensitic transformation temperatures and the mechanical behavior of SMAs. However, there is no report on the effect of gamma irradiation on transformation temperatures and thermodynamics parameters of CuZnAl SMA. Thus, we have focused on this study to know the effect of the gamma irradiation on transformation and thermodynamic parameters in a CuZnAl shape memory alloy.

2. Experimental

A ternary Cu-rich CuZnAl shape memory alloy with a nominal composition of Cu–21.6 wt.% Zn–5.6 wt.% Al. was supplied by Delta Materials Research Ltd. (Ipswich, UK). The samples cut from the alloy were annealed in the β phase field for 20 min at 820 °C for β sizing and rapidly quenched in an iced brine to obtain the β″ martensite. CuAlZn SMA samples were irradiated by gamma irradiation for different doses (10, 20, 30 and 40 kGy). The transformation temperatures of the unirradiated and irradiated samples were determined using differential scanning calorimetry (DSC). The measurements were performed with a DSC with a scanning rate of

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10 °C/min under atmospheric pressure at temperature range starting from 10 to 120 °C.

3. Results and discussion

The DSC results of the alloy for various irradiation doses are shown in Fig. 1(a–e). The transformation temperatures, i.e. the martensite transformation start (M_s), finish temperatures (M_f) and austenite transformation start (A_s), finish temperatures (A_f), have been determined from the curves, and are given in Table 1. A change in the transformation temperatures is observed due to the irradiation, and transformation temperatures shift to the lower temperatures. Thus, it is evaluated that the relative phase stability is altered by the irradiation. The changes in the A_s, A_f are due to the stabiliza-

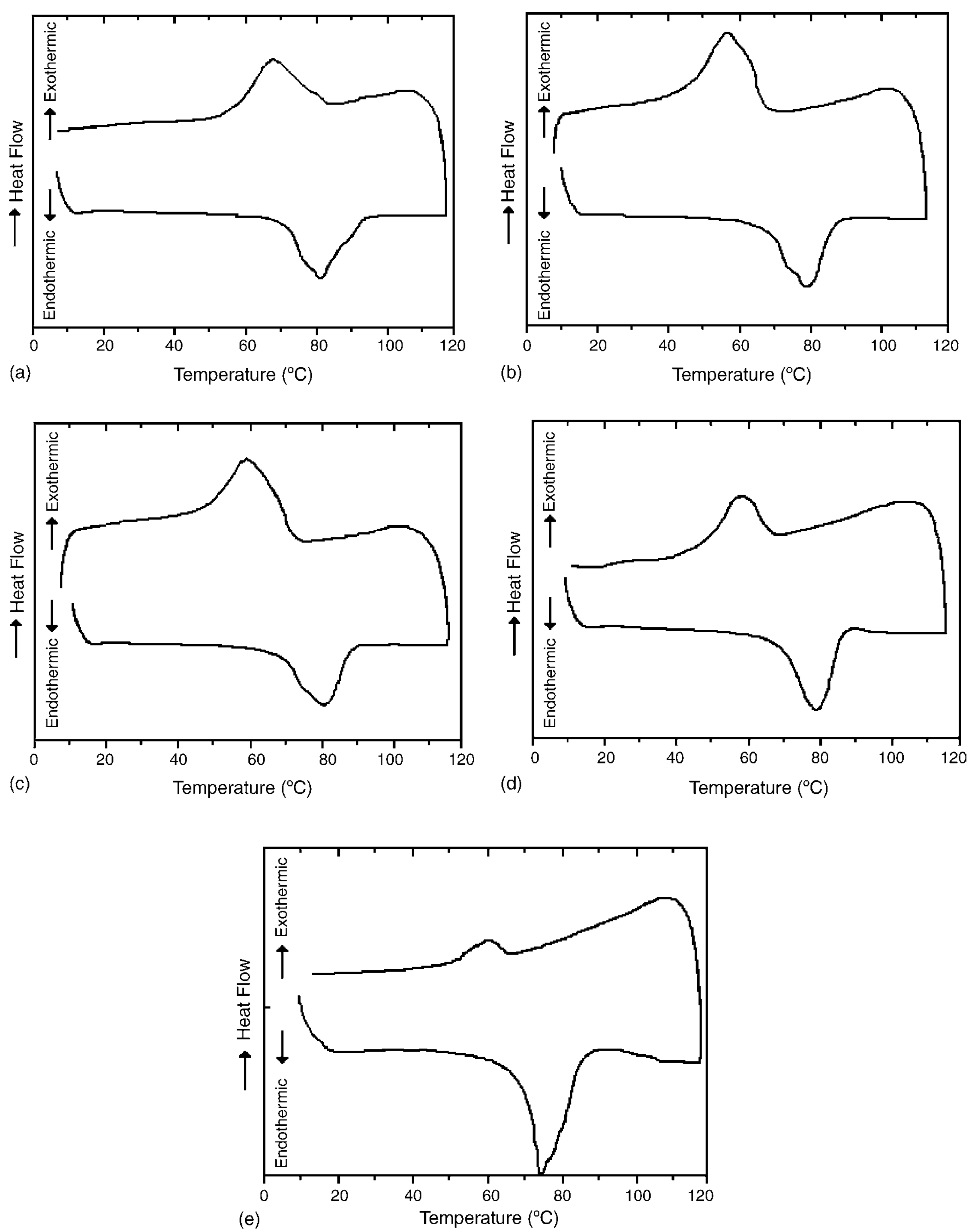

Fig. 1. DSC curves of the alloy at various doses (a) unirradiated (b) 10 kGy (c) 20 kGy (d) 30 kGy (e) 40 kGy.

Table 1
The transformation temperature parameters of the alloy at various doses

Dose (kGy)	M_s (°C)	M_f (°C)	$M_s - M_f$ (°C)	A_s (°C)	A_f (°C)	$A_f - A_s$ (°C)	$A_f - M_s$ (°C)	T_0 (°C)
0	84.0	49.4	34.6	64.3	96.4	32.1	12.4	90.2
10	75.5	43.3	32.2	62.8	93.7	30.9	18.2	84.6
20	70.6	42.8	27.8	61.0	91.1	30.1	20.5	80.8
30	68.2	43.2	25.0	60.4	89.3	28.9	21.1	78.7
40	68.1	40.3	27.8	59.1	87.6	28.5	19.5	77.8

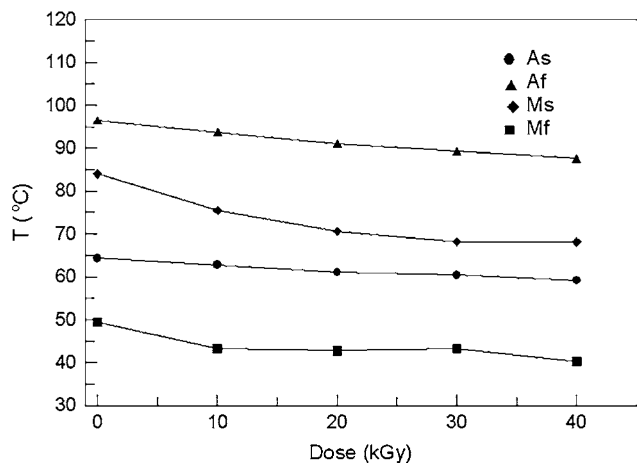

Fig. 2. Changes of transformation temperatures with the dose of gamma irradiation in CuZnAl alloy.

tion of the martensite phase. The transformation temperature dependence of the irradiation can be written as

$$T_u = a + b^n \tag{1}$$

where T_u is the transformation temperature, a the constant, b the dose rate, and n is the constant. The transformation temperatures dependence of the irradiation doses are shown in Fig. 2. The plots were fitted a linear function and n and a values were calculated from the slope and intercept of these plots (Fig. 2). The relationship between irradiation dose and transformation temperatures was experimentally determined by the following equations:

$$A_s(^\circ\mathrm{C}) = b^{1/25}(\mathrm{kGy/h}) + 4.329 \tag{2}$$

$$A_f(^\circ\mathrm{C}) = b^{1/22}(\mathrm{kGy/h}) + 4.759 \tag{3}$$

$$M_s(^\circ\mathrm{C}) = b^{1/14}(\mathrm{kGy/h}) + 4.668 \tag{4}$$

$$M_f(^\circ\mathrm{C}) = b^{1/26}(\mathrm{kGy/h}) + 3.965 \tag{5}$$

where unit of b is the kGy/h. The shifts were characterized by $A_f^{(1)} - M_s^{(0)}$, where $A_f^{(1)}$ is the end of the first transformation after irradiation and $M_s^{(0)}$ is the beginning of the transformation before irradiation [13]. It is seen that the shift varies by irradiation dose. The difference in $A_f - M_s$ can be interpreted as degree of the stabilization and the decrease or increase in ordering degree is responsible for the martensite stabilization. The stabilization process is controlled by the excess vacancy concentration and takes place via migration of vacancies. The vacancy concentration introduced during irradiation C_V can be calculated with a simple defect reaction model using the expression [14]:

$$C_{V=}(t_{ir} D_0 C_s)^{1/2} \tag{6}$$

where D_0 is the displacement rate, t_{ir} the irradiation time, and $C_s = 7 \times 10^{-7}$ is the sink density [15]. The C_V values for the alloy were calculated help of Eq. (6) and are given in Table 2. It is seen that C_V values changes with irradiation dose. When C_V values of alloy studied were compared with electron irradiation-induced stabilization in CuZnAlNi alloys, it is seen that C_V values of the alloy studied is higher than that of CuZnAlNi alloy [13]. It is evaluated that the transformation shift at saturation depends in the initial vacancy concentration. The obtained results suggest that the $A_f - M_s$ changes by irradiation and the $(A_f - M_s)$ values of martensite phase to austenite transformation increase except for 40 kGy dose, as seen in Table 1. It is found that the transformation temperatures after irradiation are smaller than that of the unirradiated transformation temperatures. The range of the phase change temperature interval changes by irradiation dose and it decreases with increasing dose. The hysteresis width $(A_f - M_s)$ varies by irradiation and then is almost constant. M_s temperature changes up to 16 °C. M_f, A_s and A_f temperatures also shift by the different amount as M_s. This implies that the hysteresis is changed. The hysteresis region of irradiated sample is wider than that of unirradiated sample. It is evaluated that the decrease in the transformation temper-

Table 2
Irradiation effect on the thermodynamic parameters of the alloy

Dose (kGy)	T_0 (°C)	$\Delta H^{M\to P}$ (J/g)	$\Delta S^{M\to P}$ (J/g °C)	$\Delta G^{P\to M}$ (J)	ΔE_e (J)	C_V	dpa
0	90.2	7.11	0.0788	−0.483	2.698	–	–
10	84.6	6.81	0.0804	−0.728	2.576	9.30×10^{-4}	1.03×10^{-5}
20	80.8	6.65	0.0823	−0.836	2.279	2.28×10^{-3}	3.11×10^{-5}
30	78.7	6.32	0.0803	−0.840	2.000	3.36×10^{-3}	4.51×10^{-5}
40	77.8	5.70	0.0732	−0.708	2.029	4.17×10^{-3}	5.22×10^{-5}

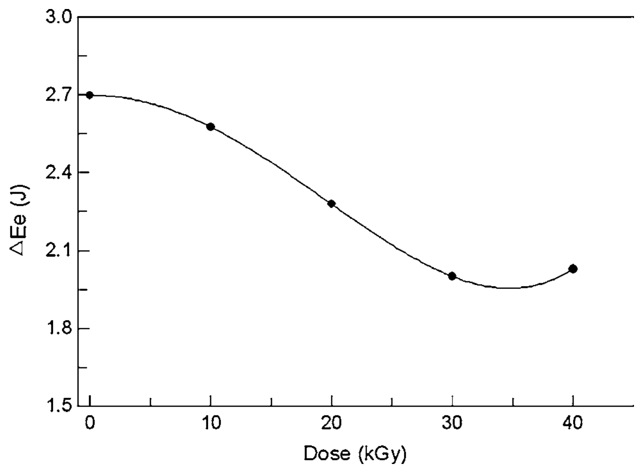

Fig. 3. Variation of elastic energy after the gamma irradiation.

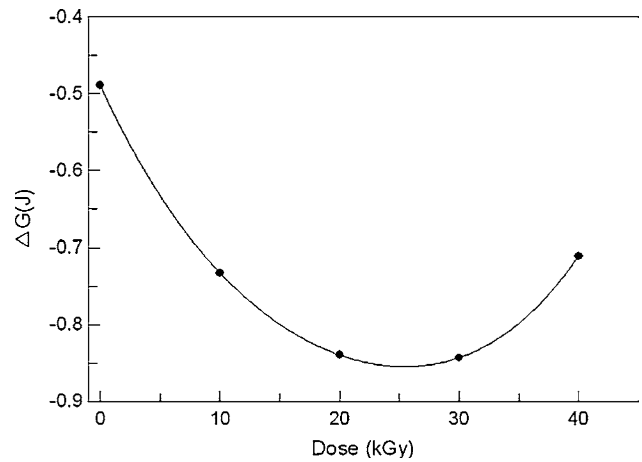

Fig. 4. Changes of Gibbs free energy with the dose of gamma irradiation in CuZnAl alloy.

atures may result from point defects and lattice imperfections produced by gamma irradiation. It is noted to discussion that gamma irradiation with 10 kGy dose has an important effect on the M_s, M_f, A_s and A_f transformation temperatures and produces a strong decrease of the transformation temperatures. The thermodynamic equilibrium temperature is decreased by gamma irradiation. Temperature M_s can be expressed as [16]:

$$M_s = T_0 + \frac{\Delta E_e}{\Delta S^{P\to M}} \tag{7}$$

where T_0 is the equilibrium temperature, ΔE_e the elastic strain energy, ΔS the entropy change. The variation of the elastic energy with gamma irradiation is shown in Fig. 3. The decrease in M_s after irradiation was assigned to the decreasing of elastic strain energy. The decrease in $M_s - M_f$ is attributed to a relaxation of ΔE_e [17,18]. The elastic strain energy shows a minimum point at 35 kGy (Fig. 3). It is found that the elastic strain energy decreased by about 27% after the gamma irradiation applied.

The transformation enthalpy, $\Delta H^{M\to P}$ for different irradiation doses was determined by means of the DSC curves given in Table 2. ΔH values are decreased with increasing irradiation doses. It is seen that $\Delta H^{M\to P}$ values are positive and $\Delta H^{M\to P}$ is referred as latent heat for the phase transformation.The Gibbs free energy for the alloy is expressed by the following relation [17]:

$$\Delta G^{P\to M} = \Delta G^{M\to P}(T_0) - \Delta G^{M\to P}(M_s) \tag{8}$$

where $\Delta H^{M\to P}$ is the Gibbs free energy for transformation from martensite to parent phase. T_0 is equilibrium temperature between the martensitic and parent phases. The $\Delta G^{M\to P}$ values for the various irradiation doses were calculated and are shown in Fig. 4. It is found that Gibbs free energy decreased by about 47% after the gamma irradiation applied. It is well-known that the equilibrium temperature, T_0 for the alloy is expressed as

$$T_0 = \frac{\Delta H^{M\to P}}{\Delta S^{M\to P}} \tag{9}$$

T_0 values for the alloy were calculate as, shown in Fig. 5. T_0 values are decreased by gamma irradiation. It is evaluated that gamma irradiation has an important effect on enthalpy and entropy of martensite or parent phase and it decreases Gibbs free energy. So, T_0 values decrease with irradiation dose. It is well-known that the equilibrium temperature T_0 between the martensitic and the parent phase is the temperature at which the Gibbs free energies of the two phases are equal.

The effect of displacement damage in a material under irradiation is an important a factor for the nuclear materials. That is why, in order to determine displacements per atom (dpa), it is important for this alloy. The standard method for calculating dpa is the modified Kinchin–Pease method [19]. The nominal dpa level was estimated [19] and is given in Table 2. This suggests that gamma irradiation leads to some observable changes on the martensitic temperatures of this alloy.

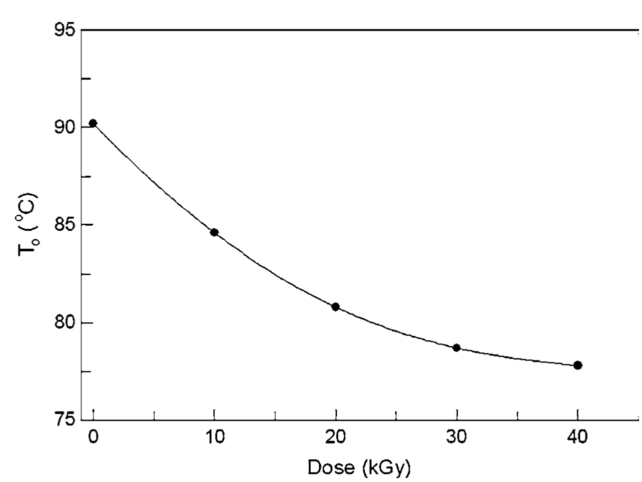

Fig. 5. Effect of gamma irradiation on the equilibrium temperature of the alloy.

4. Conclusions

The effect of the gamma irradiation on transformation temperatures and thermodynamic parameters of the CuZnAl shape memory irradiated with different doses alloy has been investigated. A change in the transformation temperatures is observed due to the irradiation and transformation temperatures shift to the lower temperatures. The temperature M_f, A_s and A_f shift by the different amount as M_s. It is found that the elastic strain energy and Gibbs free energy decreased by about 27 and 47% after the gamma irradiation respectively. When C_V values of alloy studied were compared with electron irradiation-induced stabilization in CuZnAlNi alloys, it is seen that C_V values of the alloy studied is higher than that of CuZnAlNi alloy. The nominal dpa level was estimated as $\sim 10^{-5}$.

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