



# The effects of gamma-irradiation on transformation temperatures of NiTi shape memory alloy

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## ARTICLE INFO

### Article history:

Received 2 February 2010

Received in revised form 8 March 2010

Accepted 10 March 2010

Available online 18 March 2010

### Keywords:

Shape memory alloy

Gamma-irradiation

Transformation temperatures

Gibbs free energy

## ABSTRACT

The influence of gamma-irradiation on transformation temperatures of NiTi shape memory alloy was investigated by differential scanning calorimetry. The austenite transformation temperatures shifted to higher temperatures after gamma-irradiation, whereas the martensite transformation temperatures shifted to lower temperatures. The equilibrium temperature,  $T_0$  between the martensitic and parent phases increases with increasing irradiation dose. The Gibbs free energy values,  $\Delta G^{P \rightarrow M}$  for the transformation from parent phase to martensite phase were determined and the value of  $\Delta G^{P \rightarrow M}$  increases with increasing irradiation dose up to 60 kGy. The mechanism of gamma-irradiation inducing the martensitic transformation is due to the displacements of atoms from their lattice sites produced by the accelerated gamma particles.

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## 1. Introduction

Ni–Ti-based alloys are the most important practical shape memory alloys (SMA) with excellent mechanical properties. There are many phase transformations in Ti–Ni-based alloys system, which include not only diffusionless/martensitic transformations, from which shape memory and superelastic effects arise, but also diffusional transformations. Applications for driving machine components from a remote place or connecting detachable machine elements with strong force can be realized in a limited space, so that these alloys are expected as useful functional component materials for a fusion reactor [1]. In such a case, the irradiation effects on the shape memory characteristics of these alloys are very important.

There have been several studies on the change of shape memory characteristics of TiNi and CuAlNi, CuZnAl SMAs after neutron, gamma, proton and electron irradiation [2–13]. The neutron irradiation was found to decrease the transition temperatures [4,5,13]. The proton irradiation shifts the temperatures of martensite  $\leftrightarrow$  austenite transformation of TiNi SMAs [8,11]. The transformation temperatures  $A_s$  and  $A_f$  of TiNi thin films are increased by the electron irradiation. But the irradiation has little effect on  $M_s$  and  $M_f$  ( $A_s$ ,  $A_f$  and  $M_s$ ,  $M_f$  is austenite transformation start, finish temperature and the martensitic transformation start, finish temperature, respectively) [14]. The martensitic phase is stabilized [15,16] by the irradiation in the sense that the reverse

transformation temperatures were higher than before. This is similar to the results of electron irradiated TiNi–Cu shape memory alloy [17].

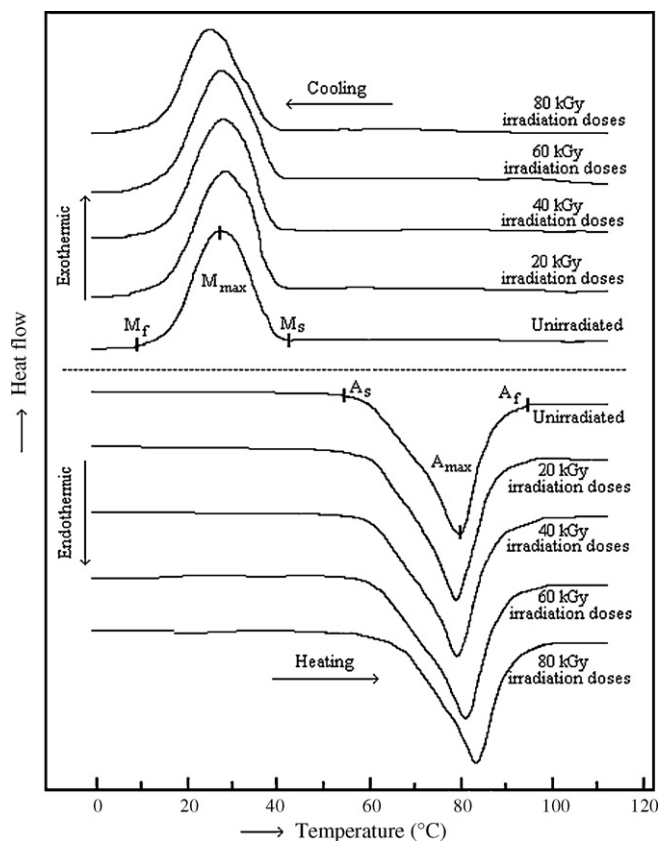
The results indicated that the irradiation has a very strong influence on the martensitic transformation temperatures and the mechanical behavior of SMAs. Thus, we have focused on this study to know the effect of the gamma-irradiation on transformation and thermodynamic parameters in a NiTi shape memory alloy.

## 2. Experimental

The NiTi alloy used in this study was supplied from the memory-Metalle GmbH, Germany. The nominal composition is Ni–44.74Ti (wt.%). Samples cut from this alloy were annealed in the  $\beta$ -phase field for 30 min at 850 °C for betasising and later rapidly quenched in iced brine in order to form the  $\beta$  martensites. Pieces of samples were irradiated using a  $^{60}\text{Co}$   $\gamma$ -source with 20 kGy ( $20 \times 10^6$  rad), 40 kGy ( $40 \times 10^6$  rad), 60 kGy ( $60 \times 10^6$  rad) and 80 kGy ( $80 \times 10^6$  rad) total doses. The samples were exposed to  $^{60}\text{Co}$   $\gamma$ -source with irradiation the dose rate of 2.12 kGy/h to obtain 20 kGy, 40 kGy, 60 kGy and 80 kGy total doses. The dose of irradiation was automatically controlled by irradiation system. The gamma-irradiation was performed Saraykoy Nuclear Research and Training Center (SANAEM), Turkey Atomic Energy Agency. The differential scanning calorimetry (DSC) measurements of unirradiated and irradiated samples (124 mg) were performed to determine the transformation enthalpies, the forward–reverse transformation temperatures of martensite  $\leftrightarrow$  austenite phase. Perkin Elmer Sapphire DSC was used with 10 °C/min heating and cooling rates in –10 and 120 °C range.

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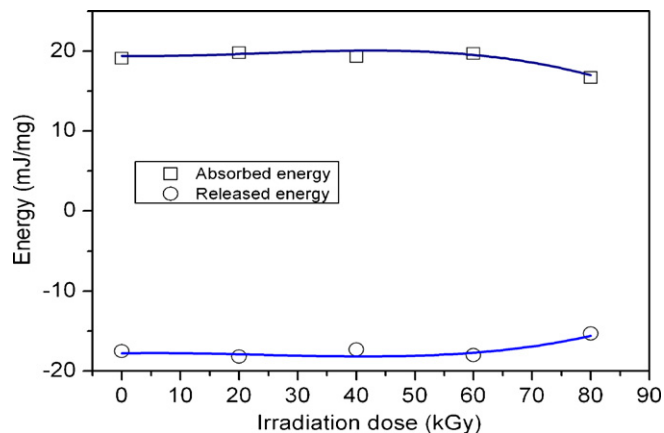


**Fig. 1.** The DSC curves for the heating and cooling rates of 10 °C/min of unirradiated and irradiated samples.

The phase transformation parameters, martensite start temperature  $M_s$ , martensite finish temperature  $M_f$ , austenite start temperature  $A_s$ , austenite finish temperature  $A_f$ , absorbed energies values during cooling and heating, maximum peak temperatures ( $A_{max}$  and  $M_{max}$ ) were automatically determined from DSC curves using a Perkin Elmer Sapphire DSC software programming. Microstructures of the alloy were investigated by Scanning Electron Microscopy (SEM) using a JSM-7001F.

### 3. Results and discussion

Fig. 1 shows the results of differential scanning calorimetry (DSC) studies of the samples before and after gamma-irradiation for 10 °C/min. The austenite and martensite temperatures of the transformation were determined from the DSC curves and are given in Table 1. During heating and cooling, a one-stage transformation is observed, namely, from the martensite (B19') to parent phase (B2). The martensitic transformation is a diffusionless first order phase transition in crystalline solids, in which atoms move cooperatively [18]. The transformation temperatures dependence of irradiation dose is shown in Table 1. As seen in Table 1, the transformation temperatures are changed due to the irradiation. The  $A_s$  and  $A_f$



**Fig. 2.** The absorbed and released energy values of the irradiated and unirradiated alloy.

transformation temperatures are increased, while  $M_s$  and  $M_f$  values are decreased with irradiation dose. This indicates that the relative phase stability is altered by the irradiation. The changes in the  $A_s$ ,  $A_f$  are due to the stabilization of the martensite phase. The hysteresis ( $A_{max} - M_{max}$ ) value for the gamma-irradiated samples is about 51.2 °C. This hysteresis is rather high and it is one of the typical characteristics of thermoelastic martensitic transformation. The relation between transformation temperatures and irradiation dose can be analyzed by the following relation [19]

$$T_t = G^{1/m} + n \quad (1)$$

where  $T_t$  is the transformation temperature,  $G$  is the irradiation dose,  $m$  is an exponent and  $n$  is a constant. The relationship between irradiation dose and transformation temperatures for NiTi alloy was experimentally found by the following equations

$$A_s (\text{°C}) = G^{1/30}(\text{kGy}) + 50.1 \quad (2)$$

$$A_f (\text{°C}) = G^{1/43}(\text{kGy}) + 88.8 \quad (3)$$

$$M_s (\text{°C}) = G^{-1/76}(\text{kGy}) + 43.5 \quad (4)$$

$$M_f (\text{°C}) = G^{-1/6}(\text{kGy}) + 88.8 \quad (5)$$

This relation indicates that the irradiation to move the martensite plates. The obtained  $m$  values are positive for austenite transformation, whereas they are negative for martensite transformation. This indicates that the  $A_s$  and  $A_f$  values increases with increase in irradiation dose, while  $M_s$  and  $M_f$  values decrease. The austenite start transformation temperature increases 3.5 °C by irradiation dose, while martensite start transformation temperature increases 2.3 °C by irradiation dose. The absorbed and released energy values of the alloy irradiated were determined and are shown in Fig. 2. The energy values change with irradiation dose. This suggests that the irradiation dose cause a decrease in the size of the martensite phase. The decrease in the energy values results in a higher driving force for the reverse transformation. The increase in the transformation temperatures of the alloys can be explained as follows, the cubic B2 structure in the parent phase is taken place in

**Table 1**

The reverse and forward transformation temperatures and the absorbed energies obtained from the heating and cooling curves in Fig. 1.

NiTi	$A_s$ (°C)	$A_{max}$ (°C)	$A_f$ (°C)	$M_s$ (°C)	$M_{max}$ (°C)	$M_f$ (°C)	$T_0$ (°C)	Absorbed energy during heating (mJ/mg)	Absorbed energy during cooling (mJ/mg)
Unirradiated	54.7	80.1	94.6	42.5	27.8	8.4	68.55	19.1	-17.5
20 kGy irradiation doses	55.5	79.3	95.4	42.1	28.9	7.9	68.75	19.8	-18.2
40 kGy irradiation doses	56.4	79.5	96.5	40.7	28.9	7.3	68.6	19.3	-17.3
60 kGy irradiation doses	57.4	80.7	97.5	41.8	27.9	7.0	69.65	19.7	-18.0
80 kGy irradiation doses	58.2	82.8	98.6	41.0	25.2	6.1	69.8	16.7	-15.3

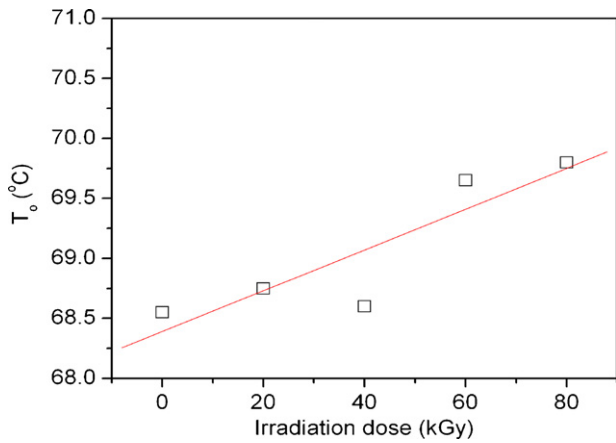


Fig. 3. Variation of  $T_0$  vs. irradiation dose for the NiTi alloy.

NiTi-based shape memory alloys. Upon phase transformation, the atoms will arrange themselves into layers with a periodic stacking order structure. The formation of titanium hydride will not hamper the movement of the interphase boundaries between the martensites and the parent phase, thus leading to the increase of transformation temperatures [11]. When the irradiated DSC curves are compared with one another, it is seen that the intensity of the DSC peak is decreased by irradiation. Thus, decrease in the intensity of peak would correspond to the amount of the martensite transformation and amount of amorphous phase. It is evaluated that the amorphous phase was observed after irradiation and DSC peak decreased in intensity with a slight shifting to lower temperatures.

The equilibrium temperature  $T_0$  between the martensitic and the parent phases is the temperature at which the Gibbs free energies of the two phases are equal [20],

$$\Delta G^{M \rightarrow P}(T_0) = G^P(T_0) - G^M(T_0) \quad (6)$$

The  $T_0$  values for the samples before irradiation and after irradiations were determined from DSC curves and are given in Table 1. Fig. 3 shows the variation of  $T_0$  vs. irradiation dose. As seen in Fig. 3, the  $T_0$  values increase with irradiation dose. This suggests that the gamma-irradiation increases the Gibbs free energies of the martensite and austenite phases and in turn, the transformation temperatures increase. The Gibbs free energies for parent phase and martensite phase transformation can be expressed by the following relation [21],

$$\Delta G^{P \rightarrow M}(M_s) = \Delta G^{M \rightarrow P}(T_0) - \Delta G^{M \rightarrow P}(M_s) \quad (7)$$

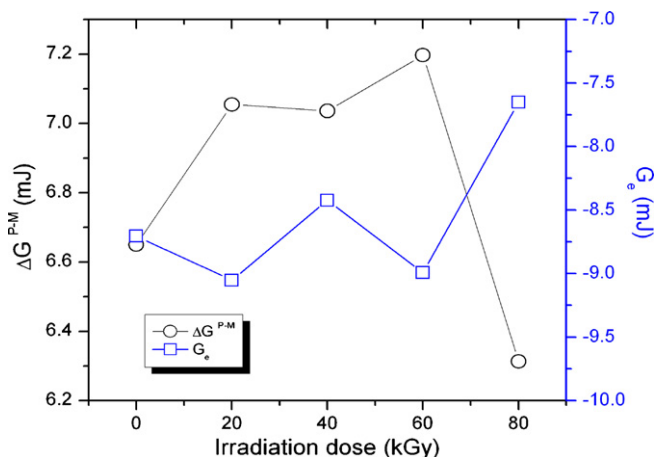


Fig. 4. Plots of  $\Delta G^{P \rightarrow M}$  and  $G_e$  vs. irradiation dose of the NiTi alloy.

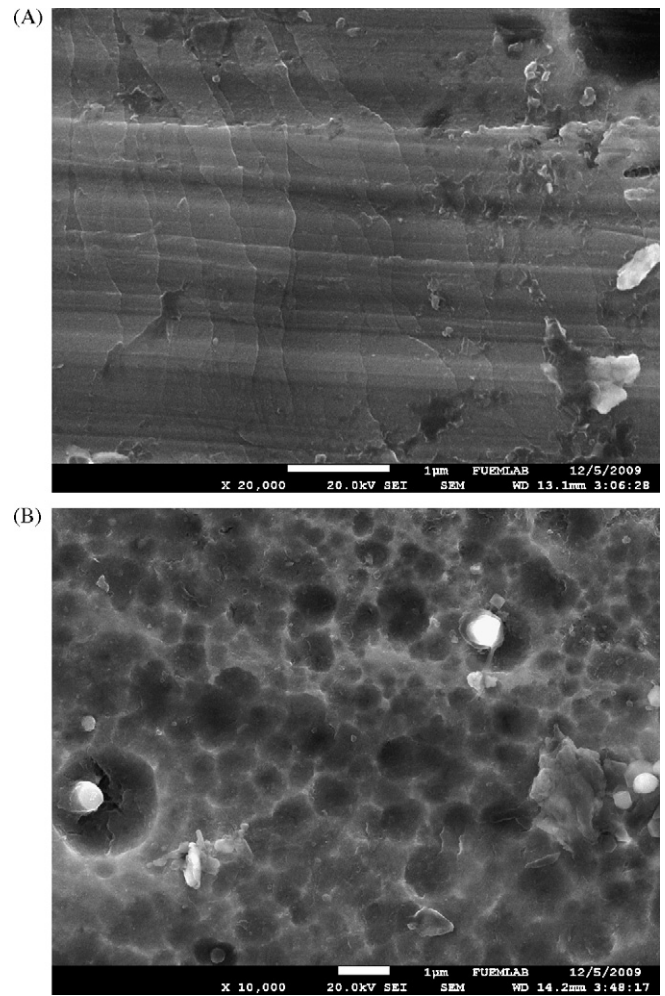


Fig. 5. SEM micrographs: (A) after thermal treatment and (B) after gamma treatment for 80 kGy.

and the elastic energy  $G_e$  stored in the self-accommodated martensitic variants is defined as [20]

$$G_e = \Delta G^{P \rightarrow M}(M_s) - \Delta G^{P \rightarrow M}(M_f) \quad (8)$$

The  $\Delta G^{P \rightarrow M}$  and  $G_e$  values were determined using Eqs. (7) and (8) and are shown in Fig. 4. The  $\Delta G^{P \rightarrow M}$  values of the samples increases with irradiation dose up to 60 kGy and then, it suddenly decreases, whereas,  $G_e$  value increases.

Fig. 5 shows SEM images of unirradiated and gamma-irradiated samples. As seen in figures, the surface photograph of unirradiated sample is changed by gamma-irradiation of 80 kGy and some defects are formed after irradiation. We can evaluate that these defects can cause an increase in the forward reverse temperature of the martensite and austenite phase transformation.

#### 4. Conclusions

The influence of gamma-irradiation on transformation temperatures of NiTi shape memory alloy films was investigated by differential scanning calorimetry. The gamma-irradiation changes austenite and martensite transformation temperatures due to the displacements of atoms from their lattice sites produced by the accelerated gamma particles.

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