The changes in transformation temperatures under stress of Cu–12.7Al–5Ni–2Mn alloy

Rasit Zengin*, Mehmet Ceylan

Department of Physics, Faculty of Arts and Sciences, Firat University, 23169 Elazig, Turkey

Abstract

The effects of the stress on shape memory properties of Cu–12.7Al–5Ni–2Mn shape memory alloy have been investigated. Applied stress increases transformation temperatures and the relationship between T_0, temperature at which Gibbs free energy of austenite equals that of martensite, and plastic deformation is linear.
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1. Introduction

Among the wide variety of alloys that exhibit the shape memory effect (SME) the most developed, as a consequence of their practical applications, are the nickel–titanium alloys and copper-based alloys, such as Cu–Zn–Al and Cu–Al–Ni [1,2]. The SME in several of these alloys was studied as a function temperature and pressure to learn about their martensitic transformation behavior. Till now, only a small number of papers have been published on the effect of hydrostatic pressure on the thermomechanical behavior of SMs [3–9]. High pressure work on shape memory alloys (SMAs) is very sparse. The role of high pressure in influencing phase transitions and in unraveling the transition mechanism is very well known [10–13]. According to the Clausius–Clapeyron equation, the volume change associated with the transformation is responsible for the shift of equilibrium temperature T_0. The most important problem is determination of T_0, since there is no way for direct measurement of this quantity and opinions differ as to what is the best approximation for the estimation of T_0 [9].

DSC is extensively used for the investigation of transition temperatures. This paper presents the effects of stress on shape memory properties of Cu–12.7Al–5Ni–2Mn shape memory alloy.

2. Experimental

The chemical composition of the alloy used in this work and electron/atom (e/a) ratio are Cu–12.7Al–5Ni–2Mn (in wt pct) and 1.57, respectively. The alloy was supplied Scientific and Technical Research Council of Turkey. Cu–12.7Al–5Ni–2Mn alloy has been solution treated β-phase condition at 900 °C for 30 min for homogenization and quenched in iced-brine to retain in the β phase. The disk-type specimens were cut from roller rod alloy. The different stresses were applied on specimens prepared with a Graseby stress apparatus. A small piece was used for DSC measurements with a Shimadzu DSC-50 instrument at a heating and cooling rate of 10 °C/min between 25 and 130 °C.

3. Results and discussion

DSC curves for forward and reverse transformation of deformed shape memory alloy are shown in Fig. 1. The transformation temperatures and enthalpy changes calculated from DSC curves are given in Table 1. The variation of the transformation temperature with pressure is shown in Fig. 2. The transformation temperature of this alloy increases with increasing pressure. The effect of the stress induced-deformation on shape memory behavior of the alloy can be determined by the following relation

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* Corresponding author. Tel.: +90-4242370000; fax: +90-4242330062.
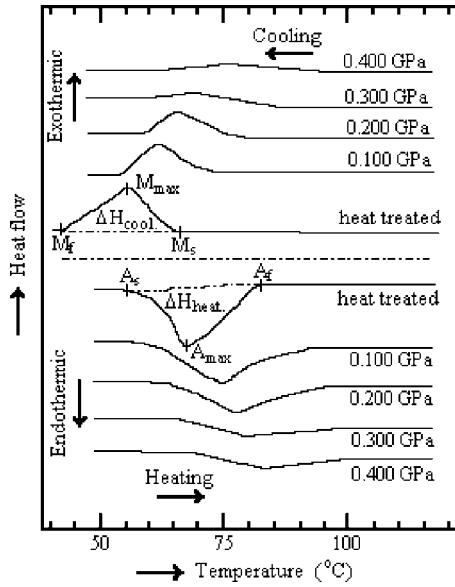*E-mail address:* rzengin@firat.edu.tr (R. Zengin).

Fig. 1. DSC curves for cooling and heating cycles.

Fig. 2. The variation of the transformation temperature with pressure.

[14,15],

$$\frac{d\sigma}{dT} = -\rho\frac{\Delta H}{\Delta\varepsilon T_0} \tag{1}$$

where $d\sigma/dT$ is the temperature coefficient of the critical pressure for transformation, given by the inverse of the alones of the lines in Fig. 2. $\Delta\varepsilon$ the amount of strain due to the pressure-induced martensite transformation, ρ the mass density, $5.2 \times 10^3\,kg/m^3$ for the alloy studied, and ΔH the enthalpy of transformation. Values of $d\sigma/dT$ are given in Table 2.

In Eq. (1), $\Delta\varepsilon$ can be obtained from measured values of ρ, ΔH and M_s. Thus, $\Delta\varepsilon$ is approximated by the following relation,

$$\Delta\varepsilon(\%) \approx 37.4\frac{M_{st} - M_{so}}{\sigma_{app}(MPa)} \tag{2}$$

where M_{st} is the martensite temperature of the thermal cycle and M_{so} the martensite start temperature of the thermal cycle. The approximation sign $\approx$ is used in Eq. (1) since the modified Clausius–Clapeyron equation has been theoretically deduced for ideally thermoelastic transformation. The values of $\Delta\varepsilon$ were calculated and are shown as a function of pressure, in Fig. 3. At pressures level lower than 300 MPa, the transformation strain is decreased and a sharp
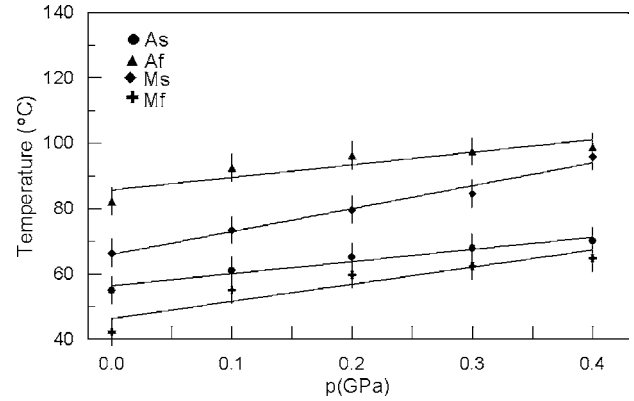
rise in the value of $\Delta\varepsilon$ is observed at pressures between 300 and 400 MPa. The transformation strain corresponds to the martensite variant at the beginning of transformation and the two-way shape memory event (TWME), the average transformation strain indicates that the martensite variants are more favorably oriented at the beginning of transformation, i.e. the variants formed at the beginning of transformation contribute more to be TWME than the variants formed at the end of the transformation.

In Eq. (1), T_0 is the temperature at which the Gibbs free energy of austenite equals that of martensite. The transition temperatures may be determined by the following relations [9],

$$M_s = \frac{T_0 - (\Delta g_{di} + e_0)}{-\Delta S_c} \tag{3}$$

$$M_f = \frac{T_0 - (\Delta g_{di}^* + e_m)}{-\Delta S_c} \tag{4}$$

$$A_s = \frac{T_0 + (\Delta g_{di}^* - e_m)}{-\Delta S_c} \tag{5}$$

$$A_f = \frac{T_0 + (\Delta g_{di} - e_0)}{-\Delta S_c} \tag{6}$$

where e_m and e_0 are the volume derivatives of the elastic energy around the M_f, A_s and M_s, A_f temperatures. Δg_{di}^* and Δg_{di} are the volume derivatives of energies dissipated at M_f, A_s and at the M_s, A_f, respectively [9]. T_0 values for this alloy are given in Table 1. Fig. 4 shows the variation of T_0 values with applied pressure.

Table 1
The transformation temperatures and enthalpy changes for transformation of the alloy

Pressure (GPa)	A_s (°C)	A_{max} (°C)	A_f (°C)	M_s (°C)	M_{max} (°C)	M_f (°C)	ΔH_{heat} (J/g)	ΔH_{cool} (J/g)	T_0^{M-P} (°C)
0	54.9	67.4	82.1	66.4	55.6	42.2	−4.78	4.31	74.25
0.100	61.0	75.1	92.4	73.4	62.5	55.1	−4.22	3.84	82.90
0.200	65.1	78.5	96.2	79.6	66.3	59.7	−3.44	2.82	87.90
0.300	67.9	80.4	97.4	84.5	69.2	62.3	−1.52	1.02	90.01
0.400	70.0	83.7	98.8	95.9	75.1	64.8	−1.32	0.70	97.35

Table 2
The some thermodynamic parameters of the alloy

Temperature	$d\sigma/dT$ (MPa °C^{-1})	$\Delta S^{\text{M-P}}$ (J/g, °C)	$\Delta H^{\text{M-P}}$ (J/g)
A_s	26.954	0.2800	23.26
A_f	26.041	0.2806	24.66
M_s	14.265	0.1496	13.46
M_f	19.083	0.2035	19.81

Fig. 5 shows the variation of ΔH with pressure induced-deformation. While the enthalpy changes on heating increase with increasing pressure, the enthalpy changes on cooling decrease with increasing pressure. The relationship between the transformation enthalpy ΔH and transformation entropy, ΔS, is given by the following relation [16],

$$\frac{\Delta H(\sigma)}{T_u(\sigma)} = \Delta S = \text{constant} \qquad (7)$$

where ΔS is the transformation entropy. T_u the transformation temperature. ΔS values are given in Table 2. It is experimentally seen that plastic deformation increases transformation temperatures. The pressure induced-plastic deformation is linearly temperature dependent as contribution of external pressure to driving force is linear. This can be explained as follows. The Gibbs free energy of the martensite and parent phase can be expressed as [17,18].

$$G_{ch}^M = H_{ch}^M - TS_{ch}^M \qquad (8)$$

and

$$G_{ch}^P = H_{ch}^P - TS_{ch}^P \qquad (9)$$

The difference in Gibbs free energy per mole between twinned martensite and parent phase under constant load
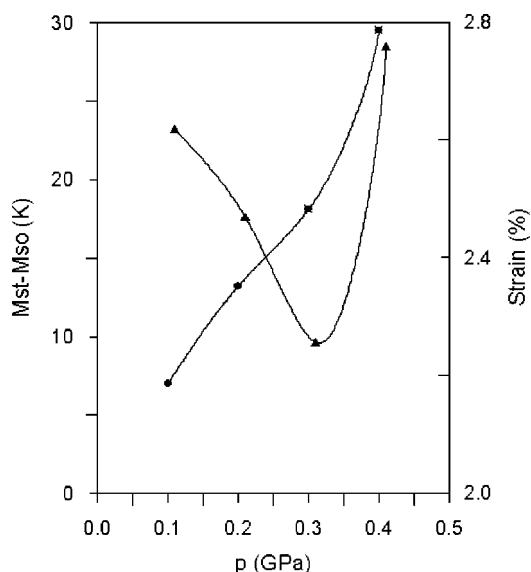

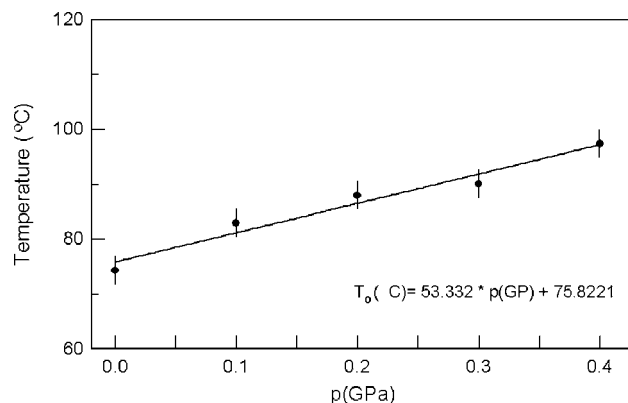Fig. 3. The variation of $(M_{st} - M_{so})$ and strain with pressure.

Fig. 4. The variation of T_0 with applied pressure for the alloy.

condition can be written as

$$\Delta G^{*M-P} = G^{*M} - G*^P = \Delta H_{ch}^{M-P} - T\,\Delta S_{ch}^{M-P}$$
$$- \sigma\varepsilon^{M-P} V_M \qquad (10)$$

where M and P indicate martensite and parent phase.

The thermodynamic parameters, ΔH_{ch}^{M-P} and ΔS_{ch}^{M-P} were calculated from the DSC curves and are given in Table 2. The shape memory behavior of the alloy is strongly dependent on applied pressure due to changing thermodynamic parameters (see Table 2). Because the amount of heat flowing from the alloy gives an indication of the martensitic transformation properties of material. The energy required forward transformation to proceed is important to determine the amount of energy system requires to undergo a transformation [19].

Since deformation occurring any pressure would shift the equilibrium temperature and hence all of the transformation domains of both forward and reserve transformations. When higher stress is applied to alloy, the alloy undergoes deformation as the slip process triggered due to introduction of a large number dislocations and also the only of variants that are in favorable direction of the pressure grow at the expense of the others. The effect of applied pressure also increases
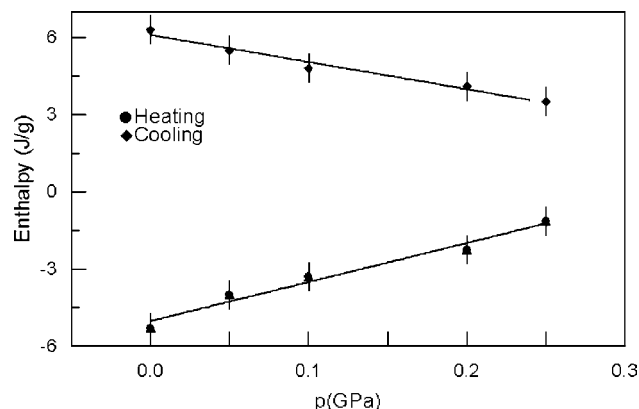

Fig. 5. The variation of the enthalpy with pressure for the alloy.

the dislocation density in the matrix. These dislocations either form the nucleation site for the martensitic phase or they may pin down the motion of the martensite plates depending on their density and interaction [19]. The shift of the transformation temperatures is due to applied stress. The more value of stress induced-deformation is higher, the higher density dislocations occur. This is reason for increase in transformation temperatures. Thus, hysteresis of higher temperatures may be changed by applied stress-induced plastic deformation. The applied pressure in the end of made cycles consists of dislocations in structure. These dislocations which result from the two way shape memory cause nucleation in the some martensitic variants and growing. This may be reason for deformation of the crystal alloy and completely causes disappearance of the shape memory. Increasing dislocation interaction with grain boundaries increases the internal pressure and has the recoverable strain starts decreasing. The grain size may also be affect on dislocations. When grain size is small, the dislocation movements may be very much hindered. It is discussed that the hydrostatic pressure affect to equilibrium temperature and thus, transformations temperatures is affected by applied pressure (Fig. 4). The nucleation and propagation of martensite in the matrix depend on the hardening mechanism caused by dislocations [13,20].

4. Conclusions

The changes in transformation temperatures under stress of Cu–12.7Al–5Ni–2Mn shape memory alloy have been investigated. The transformation temperatures increase with increasing stress. Both the relationship between the stress induced-deformation and transformation temperatures, and the relationship between T_0, temperature at which Gibbs free energy of austenite equals to that of martensite, and plastic deformation is linear.

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