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The effect of pressure on transformation temperatures and some physical parameters of Fe–32Mn–6Si–3Cr shape memory alloy

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Abstract

An experimental investigation of the effect of pressure on shape memory behavior of Fe–32%Mn–6%Si–3%Cr alloy was undertaken. There are significant differences in the Gibbs free energy, dislocation density and transformation temperatures of the alloy due to applied pressure.

Keywords: Shape memory alloy; Stress; Gibbs free energy; Dislocation density

1. Introduction

Fe–Mn–Si-based alloys have been extensively studied since the shape memory effect (SME) was discovered in a Fe–30Mn–1Si single crystal in 1982 by Sato et al. [1] and later in polycrystals in 1986 by Murakami et al. [2]. Since these alloys exhibit mainly one-way SME, they are expected to be used as material of tighteners or pipe couplings on a large scale due to their low cost and good workability. It is reported [3–5] that Fe–Mn–Si alloy containing 28–34 wt.%Mn and 4–6.5 wt.%Si, exhibit a nearly perfect shape memory effect (SME). Moreover, Cr and Ni have been improved to the Fe–Mn–Si alloy resulting in an improved SME, recently [6]. Among the classical shape memory alloys, the main feature of Fe-based shape memory alloys is to present a non-thermoelastic transformation. Thus, good shape memory properties are quite difficult to obtain. The shape memory effect is drastically changed when stress is applied. However, the martensite transformation temperatures, which are very important parameters in the performance and applications of these alloys, cannot be calculated directly from the thermodynamics of materials. The martensite start temperature, M_s and the austenite start temperature, A_s temperatures can be obtained directly by electrical resistivity, magnetization and dilatometry measurements on alloy samples.

The aim of this study is to investigate the effect of pressure on Gibbs free energy, dislocation density and transformation temperatures of a new shape memory alloy, Fe–32%Mn–6%Si–3%Cr.

2. Experimental

The alloy, Fe–32 wt.%Mn–6 wt.%Si–3 wt.%Cr, is supplied by the Scientific and Technical Research Council of Turkey. The alloy is subjected to heat treatment at 1050 °C for 30 min for homogenization and quenched in iced-brine. Sample sizes were 1 mm × 2 mm × 2 mm plate. After yield strength of the alloy was determined by tensile and stretching measurements, the different pressures (200, 300 and 400 MPa) were applied to the samples in the limit of yield strength of the alloy. No shape change was observed on samples. After applied pressures were removed, differential scanning calorimetry (DSC) measurements were performed to determine the transformation energies and the forward and reverse transformation temperatures. The experiments were carried out in the range of 25–500 °C with a heating rate of

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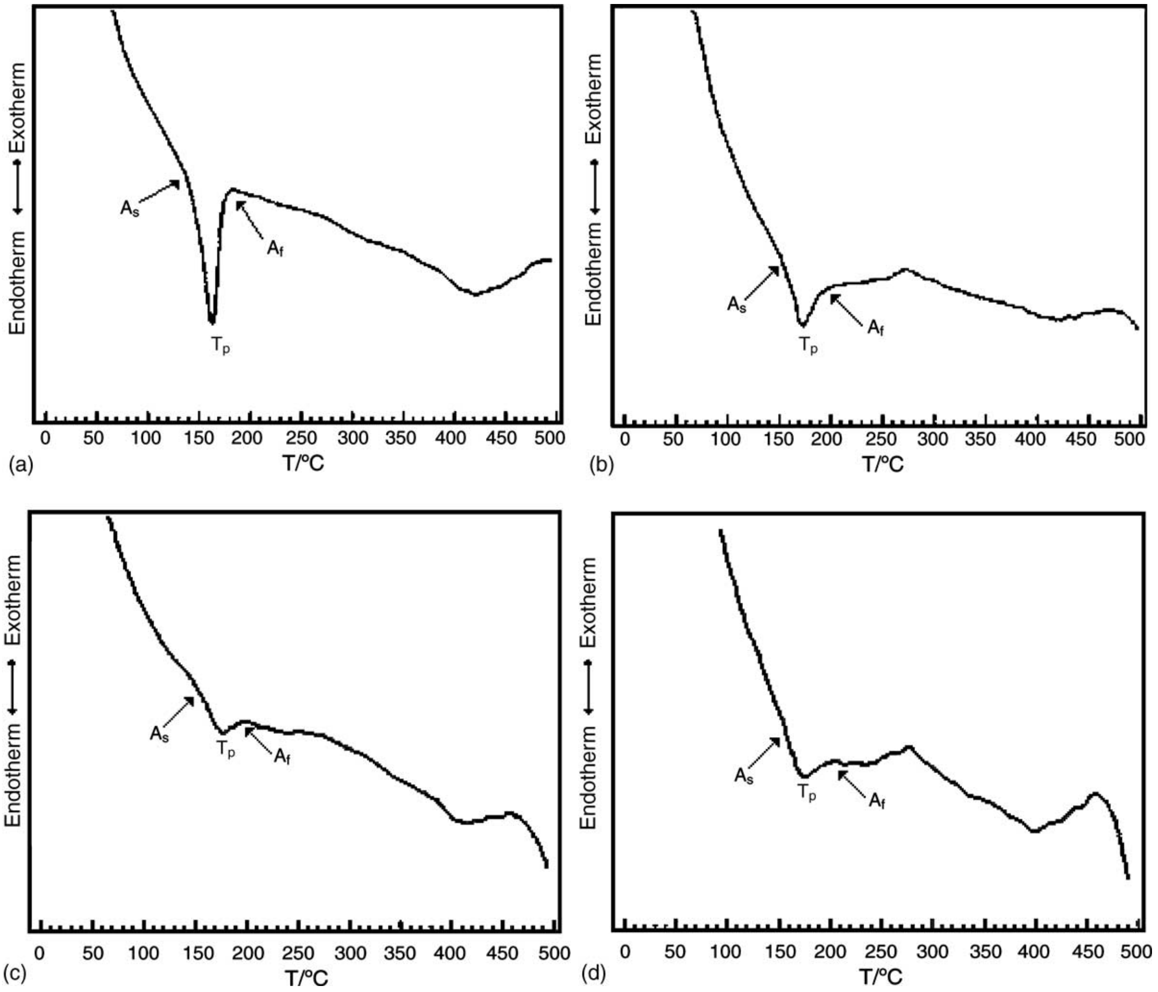

Fig. 1. The DSC curves at different pressures: (a) 0 MPa; (b) 200 MPa; (c) 300 MPa; (d) 400 MPa.

10 °C/min using a computer-controlled Shimadzu DSC-50. To identify the phases of the alloy, X-ray diffraction (XRD) patterns of alloy subjected to pressure were recorded by X-ray powder diffractometer (Rigaku Geigerflex) with Cu Kα_1 source. The parameters of the phases were determined from the XRD data with an accuracy of ±0.0003 Å.

3. Results and discussion

DSC curves of alloy subjected to pressure are shown in Fig. 1. The transformation temperatures (the austenite start temperature A_s, austenite finish temperature A_f and exothermic maximum peak temperature, T_p) shift to higher temperatures with increasing pressure. The changes are almost linear, as shown Fig. 2. It is well known that applied pressure has an important effect on the austenite transformation. Under pressure the martensite phase produces changes in the transformation temperatures and the endothermic peak observed in DSC curves is asymmetrical. The difference in A_s and A_f temperatures is shown in Fig. 3. The results indicate that the relative phase stability is altered by pressure. Thus, there is average pinning of the movement of the parent interface. The shifts in A_s and A_f are due to stabilization of the martensite phase. The pressure has an important effect on the enthalpy of the transformation. The values of the enthalpy calculated from the area under the endothermic peak using (software of DSC equipment) are shown in Fig. 4. The enthalpy decreased with increasing pressure due to plastic deformation

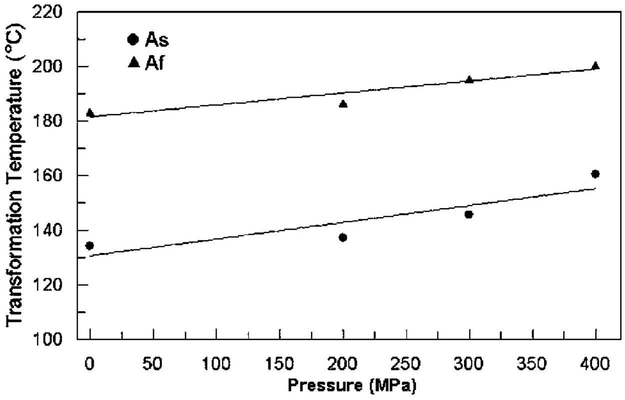

Fig. 2. The variation of transformation temperatures with applied pressure.

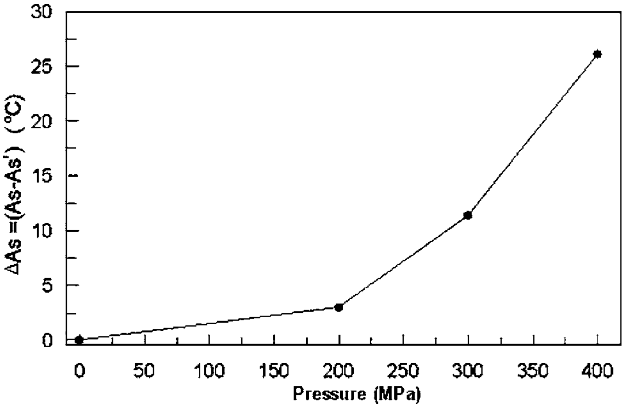

Fig. 3. The variation of ΔA_s with applied pressure.

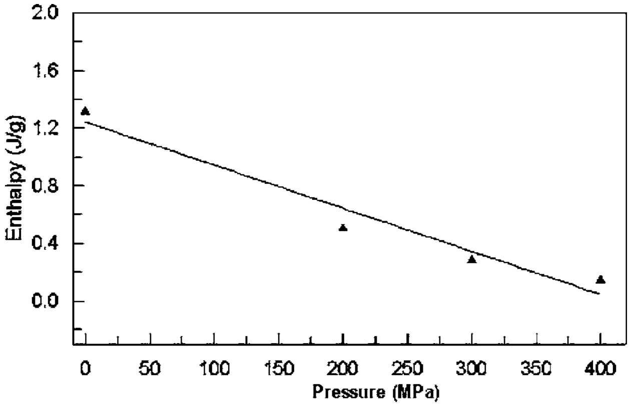

Fig. 4. The variation of transformation enthalpy with applied pressure.

of martensite. The X-ray patterns of the alloy subjected to pressure are shown in Fig. 5a–d. The phases γ, ε and α are shown in the figures. Fig. 5c includes all the phases, but Fig. 5a, d and b include only γ and γ–ε, respectively. The lattice parameters of the phases are given in Table 1. The width of the endothermic peak changes with pressure, leading to a conclusion that the endothermic peak width depends on elastic energy.

The Gibbs free energy for the alloy can be expressed as [7]

$$\Delta G_{\mathrm{ch}}^{\mathrm{M-P}} = \Delta H_{\mathrm{ch}}^{\mathrm{M-P}} - T\Delta S_{\mathrm{ch}}^{\mathrm{M-P}} - \sigma\varepsilon^{\mathrm{M-P}} V_{\mathrm{m}} \tag{1}$$

where $\Delta G_{\mathrm{ch}}^{\mathrm{M-P}}$ is the Gibbs free energy, $\Delta H_{\mathrm{ch}}^{\mathrm{M-P}}$ is the enthalpy and $\Delta S_{\mathrm{ch}}^{\mathrm{M-P}}$ is the entropy which was calculated from the values given in Table 2. Here the subscript "ch" refers to the chemical contribution to the Gibbs free energy and superscript "M–P" indicates the difference between martensite and parent phase. σ is the applied stress and V_{m} is the volume change. The Gibbs free energy for the alloy was obtained from the values given in Table 2 via Eq. (1). The Gibbs free energy changes due to the additional energy of the volume changed, when pressure is applied to the alloy. The variation of the Gibbs free energy with temperature is shown in Fig. 6. The

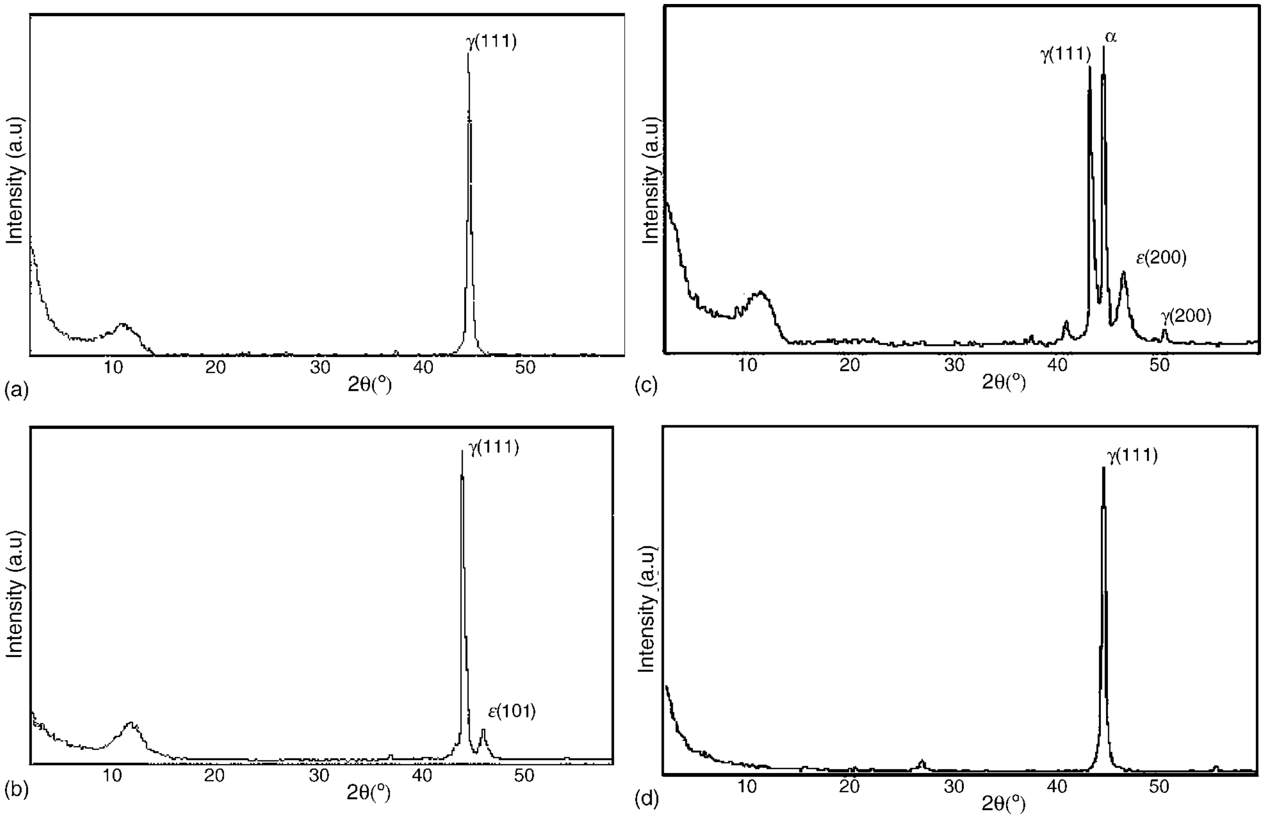

Fig. 5. The X-ray patterns of the alloy at different pressures: (a) 0 MPa; (b) 200 MPa; (c) 300 MPa; (d) 400 MPa.

Table 1
Lattice parameters of phases for the alloy

γ, *a* (Å)	ε, *a* (Å)	ε, *c* (Å)	ε, *c*/*a* (Å)
3.5998	2.5255	4.2558	1.6851

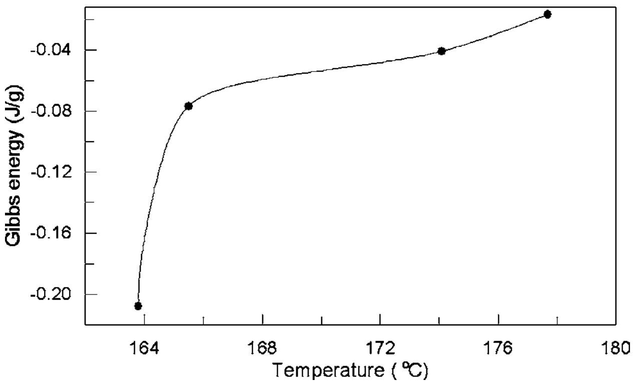

Fig. 6. The variation of total Gibbs free energy with temperature.

Gibbs energy of austenite in the alloy is increased by pressure because of the negative volume of the austenite to martensite reaction. The volume change associated with austenite transformation was also calculated by the following relationship [8]

$$\Delta G(A_{\rm s},0)-\Delta G(A_{\rm s0},0)=-\varepsilon_0\sigma \qquad (2)$$

where $\Delta G(A_{\rm s0},0)$ is the difference in Gibbs chemical free energy between austenite and martensite phase under no pressure. $\Delta G(A_{\rm s},0)$ is the difference in Gibbs chemical free energy between austenite and martensite phase under pressure. ε_0 indicates the volume change associated with the austenite transformation. The ε_0 values for the alloy were calculated via Eq. (2) and are given in Table 2. The ε_0 values increase with increasing pressure. This suggests that the applied pressure increases the volume change associated with the austenite transformation of the alloy.

The difference between $A_{\rm s}$ and $A_{\rm f}$ is related to the elastic energy $G_{\rm e}$ stored in the martensite by [9,10]

$$G_{\rm e}=\ \Delta G^{\rm M-P}(A_{\rm s})-\Delta G^{\rm M-P}(A_{\rm f}) \qquad (3)$$

The $G_{\rm e}$ values for the alloy were calculated and are given in Fig. 7. When pressure was applied to alloy, $G_{\rm e}$ values decrease with temperature. These changes may be due to the stabilization of the martensite phase with respect to the parent phase.

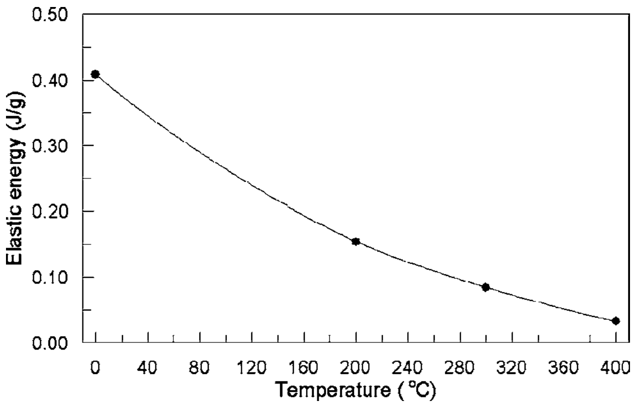

Fig. 7. The elastic energy dependence on the temperature.

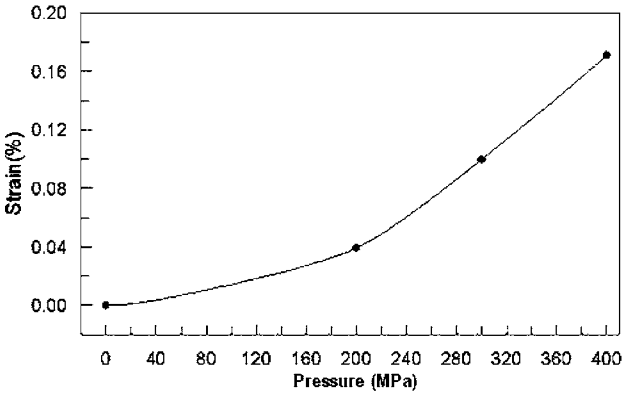

Fig. 8. The variation of the strain with applied pressure.

On the other hand, the relationship between pressure and the $A_{\rm s}$, $A_{\rm f}$ transformation temperatures for the alloy can be expressed by the following Clausius–Clapeyron equation [11]

$$\frac{{\rm d}(A_{\rm s})}{{\rm d}\sigma}\approx\frac{\varepsilon^{\rm M-P}\,A_{\rm s}(\sigma)}{\rho\,\Delta H^{\rm M-P}(\sigma)} \qquad (4)$$

where $\varepsilon^{\rm M-P}$ is the strain associated with the transformation, σ is the pressure, ρ is the density of the alloy, ΔH is the transformation energy. In Eq. (4), $\varepsilon^{\rm M-P}$ can be obtained from measured values of ρ, ΔH and $A_{\rm s}$. Thus, $\varepsilon^{\rm M-P}$ is approximated by the following relation:

$$\varepsilon^{\rm M-P}\,(\%)\approx 2.62\frac{A_{\rm s}({\rm K})-A_{\rm s0}({\rm K})}{\sigma({\rm MPa})} \qquad (5)$$

where $A_{\rm s}$ (K) is the austenite start temperature under pressure and $A_{\rm s0}$ (K) is the austenite start temperature under no pressure. The variation of the strain with pressure is shown in Fig. 8. The $\varepsilon^{\rm M-P}$ corresponds to the martensite variation

Table 2
The some physical parameters of the alloy

σ (MPa)	$A_{\rm s}$ (°C)	$A_{\rm f}$ (°C)	$T_{\rm p}$ (°C)	T_0 (°C)	$\Delta H^{\rm M-P}$ (J/g)	ε_0 (J/g Pa)	δ ($\times10^{16}$ lin m^{-2})	$\Delta S^{\rm M-P}$ (J/g °C)
0	134.2	183.1	163.8	158.8	1.32	0	4.08	0.00835
200	137.2	186.4	165.5	161.9	0.51	−0.077	4.71	0.00315
300	145.6	195.2	174.1	170.5	0.29	−0.041	4.99	0.00170
400	160.3	200.3	177.7	179.6	0.15	−0.017	7.55	0.000835

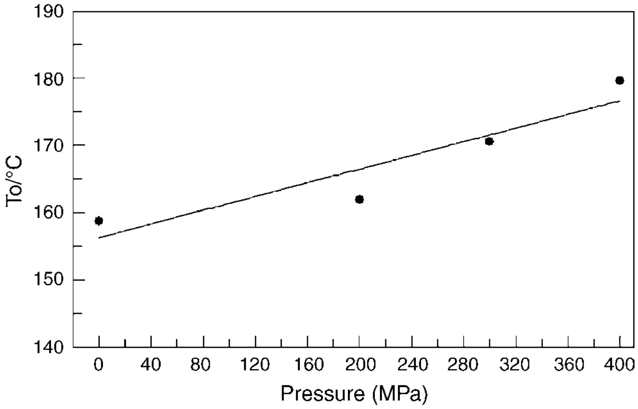

Fig. 9. The variation of T_0 with applied pressure.

formed at the beginning of transformation. It is observed that $\varepsilon^{\mathrm{M-P}}$ values of the alloy increase with the pressure. This suggests that the increase in pressure has the effect of conversion of more and more residual austenites and furthermore, it has effect of causing large shift in transformation temperatures. The effect of the pressure is to increase the dislocation density. The dislocation density δ for the alloy was calculated [12] and is given in Table 2. It is seen that the dislocation density increases with increasing pressure. The variants formed at the beginning of transformation contribute more to the shape memory effect than the variants formed at the end of the transformation. The entropy change ΔS for the alloy is expressed by the following relation:

$$\Delta S^{\mathrm{M-P}} = 2.303 C_p \log\left(\frac{T_2}{T_1}\right) \tag{6}$$

where C_p is the heat capacity and T_1 and T_2 are the characteristic peak temperatures. The $\Delta S^{\mathrm{M-P}}$ values were calculated using C_p values obtained from the DSC curves and peak temperatures. The calculated values are given in Table 2. It is seen that $\Delta S^{\mathrm{M-P}}$ values decrease with applied pressure. This suggests that disorder in the alloy increases with pressure. On the other hand, the relationship between transformation energy and thermodynamic equilibrium temperature can be written as

$$T_0 = \frac{\Delta H^{\mathrm{M-P}}(\sigma)}{\Delta S^{\mathrm{M-P}}(\sigma)} = \frac{M_s + A_f}{2} \tag{7}$$

where $\Delta S^{\mathrm{M-P}}$ is the entropy change defined in Eq. (6) and T_0 is the temperature at which the Gibbs free energy of austenite equals that of martensite. The T_0 values were calculated using Eq. (7). The thermodynamic equilibrium temperature T_0 of martensitic increases by applied pressure (Fig. 9).

4. Conclusions

The effect of pressure on Gibbs free energy, dislocation density and transformation temperatures of Fe–32Mn–6Si–3Cr shape memory alloy was investigated. The transformation temperatures and investigated physical parameters of the alloy changed by applied pressure. It is also found that the applied pressure contributes to Gibbs free energy ΔG and elastic energy G_e and dislocation density.

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