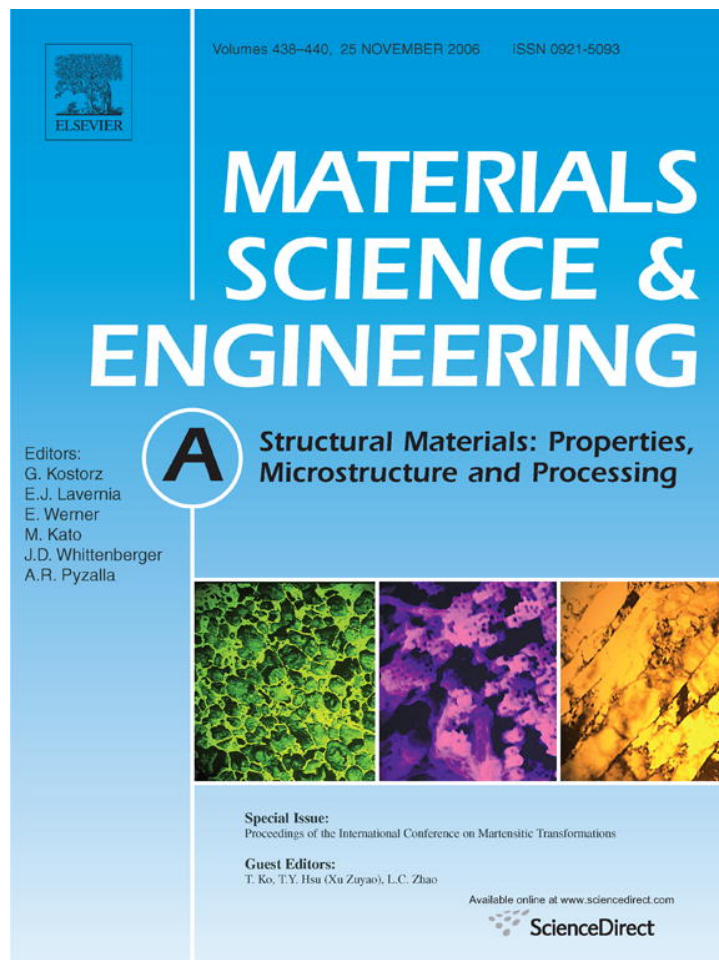


Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.



This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

Study on elastic constant softening in stress-induced martensitic transformation by molecular dynamics simulation

X.D. Ding^{a,b,*}, T. Suzuki^{a,c}, J. Sun^{a,b}, X. Ren^{a,b,c}, K. Otsuka^{a,c}

^a Multidisciplinary Materials Research Center, Xi'an Jiaotong University, 710049 Xi'an, PR China

^b State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, 710049 Xi'an, PR China

^c National Institute for Materials Science, Tsukuba 305-0047, Japan

Received 8 May 2005; received in revised form 27 October 2005; accepted 20 December 2005

Abstract

Precursor phenomena are critical issues for martensitic transformation, as they provide important clues for understanding the origin of the transformation and the structure of transformation products. Prior to temperature-induced martensitic transformation, it has been widely recognized for a long time that the basal plane shear modulus C' ($= (C_{11} - C_{12})/2$) of the parent phase decreases with approaching transformation temperature. On the other hand, martensitic transformation can also be induced by stress. But little is known about whether similar precursor phenomenon also exists prior to such a stress-induced martensitic transformation (SIM). In the present study, we used molecular dynamics method to simulate the precursory stage of a stress-induced martensitic transformation. A new method for calculating the elastic constants C' prior to SIM was proposed. The relationship between C' and applied stress at different temperatures was calculated. Our results showed that the softening of elastic constant C' is a common feature for both temperature and stress-induced martensitic transformation. For stress-induced martensitic transformation, the critical stress to induce the transformation increases with increasing temperature and obey Clausius–Clapeyron relationship; at a given temperature, C' decreases with the applied stress approaching the critical stress.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Stress-induced martensitic transformation; Elastic constant softening; Molecular dynamics simulation

1. Introduction

Martensitic transformation (MT) is defined as a displacive, diffusionless first-order transformation from a high-symmetry phase at high temperature to a low-symmetry phase (martensite) at low temperature. MT has been extensively studied for decades because of its importance in metallurgy and its key role in shape memory phenomenon.

An interesting feature of martensitic transformation in shape memory alloys is the existence of precursor phenomena [1,2]. For temperature-induced martensitic transformation, it is well known that they are a consequence of weak restoring forces in specific crystallographic directions that announce the possibility of a dynamical instability. Commonly, these systems have a low lying transverse TA₂ phonon branch together with a low value of the corresponding elastic constant C' ($= (C_{11} - C_{12})/2$); both the whole branch and the elastic constant soften with decreasing

temperature. These phenomena have been studied in Ni–Ti [3–6], Ni–Al [7,8], Au–Cd [9], and other body-centered cubic (bcc), based alloys [10].

On the other hand, stress can also induce martensitic transformation. However, little is known whether or not any precursor phenomena exist prior to a stress-induced martensitic transformation (SIM). In this paper, we mainly investigate the possibility of the elastic constant softening prior to SIM. In studying the precursory softening phenomena, for the temperature-induced martensitic transformation, elastic constants were measured with rectangular parallelepiped resonance and the pulse-echo ultrasonic method [4–6,11]. However, due to the difficulty of measurement, they are rarely applied for SIM.

Owing to the rapid progress of computers, molecular dynamics simulation (MD) is becoming a powerful tool to reveal the microscopic mechanism of MT. So far, most researches have focused on temperature-induced martensitic transformation [12–14], and there is no work done for SIM to our knowledge.

In the present study, a new method for calculating the elastic constants C' prior to SIM was proposed. By using molecular

* Corresponding author. Tel.: +81 29 82665236; fax: +81 29 82665114.
E-mail address: dingxd@mail.xjtu.edu.cn (X.D. Ding).

dynamics simulation, we simulated the precursory stage of a stress-induced martensitic transformation, and studied the relationship between C' and applied stress at different temperature. To the authors' knowledge, such work has not been reported before.

2. Analytical criterion of elastic constants

A solid body changes its shape when subjected to a stress. Provided the stress is below the elastic limit, the Hooke's law for a crystal is written as

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}, \quad (1)$$

where C_{ijkl} is the elastic stiffness, a fourth-rank tensor. In general, for cubic crystal, the independent number of elastic stiffness component reduced to three, i.e. C_{11} , C_{12} and C_{44} .

If uniaxial stress is applied in $[001]$ direction, we can obtain the following equations by derivation:

$$\frac{\sigma_{11}}{\varepsilon_{11}} = \frac{C_{11}^2 + C_{11}C_{12} - 2C_{12}^2}{C_{11} + C_{12}}, \quad (2)$$

$$\frac{\varepsilon_{12}}{\varepsilon_{11}} = -\frac{C_{12}}{C_{11} + C_{12}}, \quad (3)$$

where σ_{11} , ε_{11} are the stress and strain in $[001]$ direction, respectively, and ε_{12} is the corresponding strain in $[010]$ or $[100]$ direction. Eqs. (2) and (3) are the implicit expressions of C_{11} and C_{12} .

Furthermore, C' can be expressed as

$$C' = \frac{C_{11} - C_{12}}{2}. \quad (4)$$

By combining Eqs. (2)–(4), C' can be obtained if σ_{11} , ε_{11} and ε_{12} are given. In the present paper, a commercial software named MATLAB5.3 was used to solve Eqs. (2)–(4).

3. Molecular dynamics simulation

3.1. Computational modeling

SIM in the alloy with completely ordered B2 structures is studied with the help of commercial software named Materials Explorer2.0, which is based on the Parrinello–Rahman method [15]. However, for lacking of a proper potential function, this software cannot simulate the martensitic transformation. In this work, special 8-4 Lennard–Jones potential V_{ab} , which was proposed by Suzuki and Shimono [16] to describe the interatomic interaction for binary B2 alloys, was introduced into the software to simulate the martensitic transformation. The expression for V_{ab} can be written as follows:

$$V_{ab}(r) = e_{ab} \left\{ \left(\frac{r_{ab}}{r} \right)^8 - 2 \left(\frac{r_{ab}}{r} \right)^4 \right\}, \quad (5)$$

V_{ab} is characterized by two parameters e_{ab} and r_{ab} , which represent the bond strength between atoms and the atomic size or molar volume, respectively. To model Ti–Ni, the values of these parameters are set according to the experimental data on molar

Table 1
Parameters in Eq. (5)

r_{11} (1E–10 m)	1.0000
r_{22} (1E–10 m)	0.8494
r_{12} (1E–10 m)	0.8947
e_{11} (1E–27 J)	1.13375
e_{22} (1E–27 J)	1.03387
e_{12} (1E–27 J)	1.24900

volumes, cohesive energy and heat of formation of Ti, Ni and B2 phase of Ti–Ni alloy as shown in Table 1.

Although the molecular dynamics study based on the simple two body potential given by Eq. (5) could not reproduce all delicate aspects of the martensitic transformation particular in Ti–Ni alloys as it should be, it had been proved that this potential has been useful in reproducing the major characteristics of the martensitic transformation [16].

Furthermore, the isothermal-isobaric ensemble was adopted. As the perfect crystal structure of the TiNi alloy model has a B2-type lattice, the initial MD cell was installed in a cubic box containing 3456 atoms (1728 Ti and 1728 Ni). To avoid the existence of the free surface in the simulated MD cell, periodic boundary conditions were acted in three dimensions.

3.2. Temperature-induced martensitic transformation

To begin with the simulation of SIM, the transformation temperatures of the ensemble should be first determined, i.e., M_s (martensitic-start temperature upon cooling), M_f (martensitic-finish temperature upon cooling), A_s (reverse-transformation-start temperature upon heating) and A_f (reverse-transformation-finish temperature upon heating). So the simulation of martensitic transformation during temperature cycles was first done.

The simulation started with an ensemble of parent phase (B2 structure) at 300 K; after 20 picoseconds (ps) thermal holding, cooling procedure started and the ensemble was cooled from 300 to 0.1 K in 60 ps. The cooling rate was about 5×10^{12} K/s. In the subsequent 40 ps, the temperature of the system was kept at 0.1 K to get the equilibration of the low temperature phase. Then the ensemble was heated up to 300 K again in 60 ps. The variation of temperature with time was shown in Fig. 1.

The Parrinello–Rahman cell axis lengths (a , b , c), which are related to the size and shape of the unit cell of the alloy crystal, are shown as a function of time in Fig. 1. It can be seen that the value of lattice constants in three axes keep almost the same until the temperature (T) reached to 196 K, which means the B2 structure (parent phase) is stable when the temperature is higher than 196 K. When the system was cooled from 196 to 189 K, the lattice constants changed abruptly, and B2 structure immediately transformed into the close-packed structure labeled $L1'_0$ [16]. When temperature was further cooled to 0.1 K, the values of lattice constants changed slightly, this means that $L1'_0$ structure should be stable at this level of temperature. When the system was heated to 249 K again, the values of lattice constants again

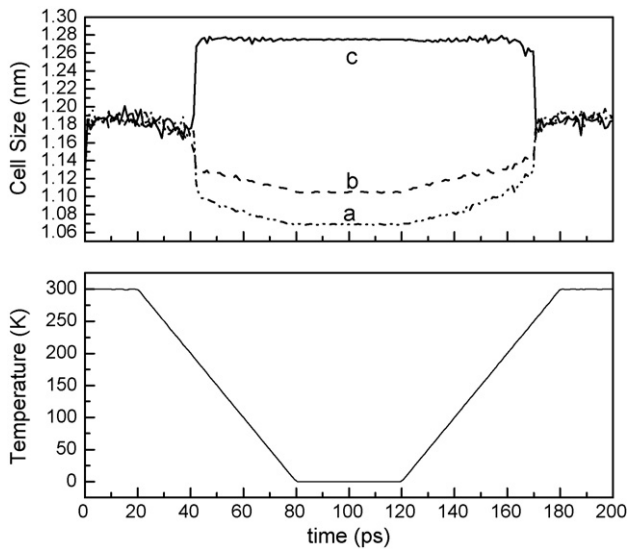


Fig. 1. The change of the Parrinello–Rahman cell axis lengths (a , b , c) and temperature are shown as a function of time. The cell is related to the size and shape of the unit cell of a completely ordered B2 crystal with 3456 atoms.

changed suddenly, and this sudden variation finished at 254 K. On further heating, value of lattice constants remained stable and expanded continuously.

As can be seen in Fig. 1, by introducing a proper potential function, this software can successfully simulate temperature-induced martensitic transformation. Furthermore, the average M_s temperature for four runs of the B2 to $L1_0''$ transformation turns out to be 196 K, the corresponding A_s temperature is 249 K, while the average M_f temperature is 189 K, and the average A_f temperature is 254 K.

3.3. Uniaxial stress-induced martensitic transformation

Initially the temperatures of the ensemble were cooled from 300 K to a given temperature in 20 ps, which is higher than M_s , and were “aged” for 20 ps to establish equilibrium. Then an external compressive stress (-50 MPa) was applied along $[001]$ direction every 20 ps. The variations of cell size and external stress with time were shown in Fig. 2.

As we known, when a martensitic system is loaded over M_s point, superelasticity occurs. It is clear from Fig. 2 that the superelasticity was simulated successfully. To facilitate the descriptions below, the martensitic-transformation-start stress upon loading is defined as critical stress (σ_s), which was shown in Fig. 2.

When a uniaxial compressive stress was applied along $[001]$ direction of the ensemble, there is a contraction in the $[001]$ direction and an expansion in $[010]$ and $[100]$ direction. This elastic deformation behavior continues until the applied stress reach to the critical stress, which is 570 MPa at 260 K for the ensemble in the present study. However, as shown in Fig. 2, the vibrations of lattice constants prior to SIM are much higher than that of temperature-induced martensitic transformation, so it is difficult to obtain the strain (ε_{11} and ε_{12}) corresponding to the applied stress directly.

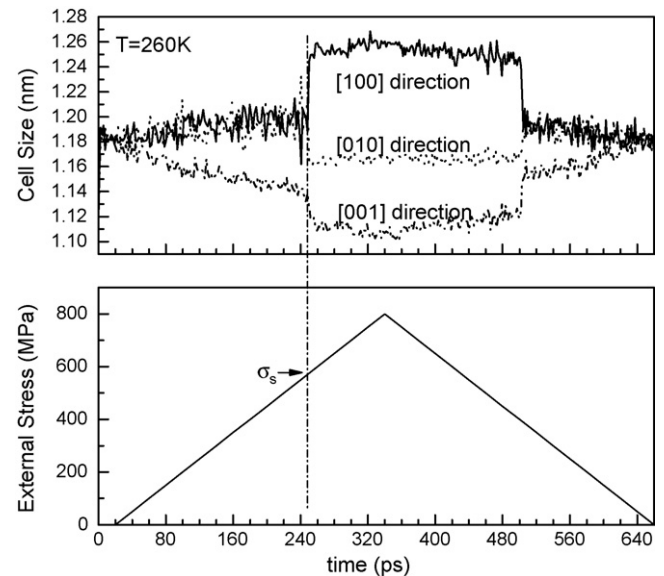


Fig. 2. The change of the Parrinello–Rahman cell axis lengths and the uniaxial compressive stress (along $[001]$ direction) as the function of time. The cell is related to the size and shape of the unit cell of a completely ordered B2 crystal with 3456 atoms.

In the present MD simulation, a long run of 2000 time steps was carried out for a given loading. All the parameters (ε_{11} and ε_{12}) corresponding the applied stress were calculated with the last 1000 time steps of this run. Furthermore, the following methods were used to deduce the scattering of calculation. Firstly, the elastic deformation behavior in $[100]$ and $[010]$ direction should be the same when a uniaxial stress is applied in $[001]$ direction of the ensemble, so the value of ε_{12} was calculated by averaging the strain in $[100]$ direction and $[010]$ direction. Secondly, a method of 10 data point smoothing was used to smooth ε_{11} (ε_{12}) versus time curves. Although the number of data points chosen for the smoothing affects the absolute values of ε_{11} (ε_{12}), experimentation with different number of smoothing was not found to invalidate the trends of C' we report here.

The relationship between elastic constant C' and external stress is shown in Fig. 3. It can be seen that C' exhibit softening towards critical stress σ_s , and the softening is non-linear for different temperatures. This is similar to that of temperature-induced martensitic transformation.

Furthermore, C' increase with increasing temperature at a given applied stress, and C' at higher temperature shows higher value in the vicinity of the critical stress σ_s . This explains the higher critical stress is needed at higher temperature, because a lower C' indicates a smaller resistance to the shear transformation.

4. Comparison with thermodynamic theory

A thermodynamic method to analyze the effect of stress on MT temperature is the use of the Clausius–Clapyeyron relationship, the relation for a uniaxial stress is written as

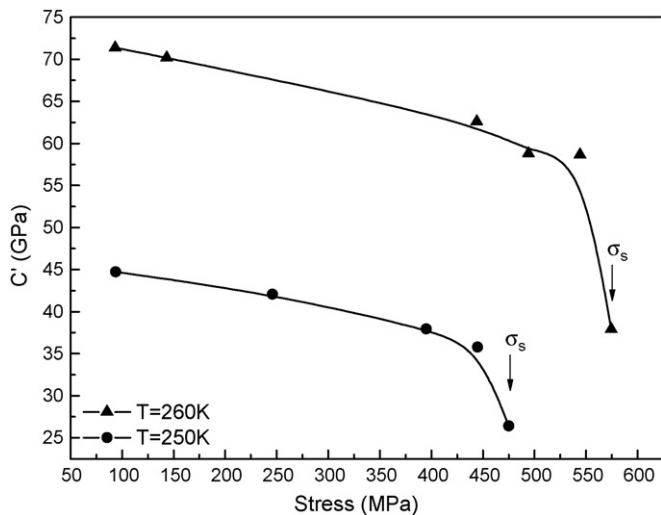


Fig. 3. Calculated elastic constant C' as the function of applied stress.

follows [17]:

$$\frac{d\sigma}{dT} = -\frac{\Delta H_V}{T_0(0)\Delta\varepsilon}, \quad (6)$$

where ΔH_V is the enthalpy change of the transformation per unit volume, σ a uniaxial stress and $\Delta\varepsilon$ a transformation strain. $T_0(0)$ is the temperature where $\Delta G^{P \rightarrow M} = 0$ ($\Delta G^{P \rightarrow M}$ is the chemical free energy change per mole for the parent-to-martensitic transformation). Strictly speaking, this equation applies for the equilibrium temperatures, but may be applied for the M_s temperature as well, if the critical driving force for the transition is independent of temperature and stress [17].

Considering the applied stress is zero at M_s point, the solution of Eq. (6) can be written as:

$$\sigma = -\frac{\Delta H_V}{T_0(0)\Delta\varepsilon}(T - M_s). \quad (7)$$

For the MD simulation in the present study, $M_s = 196$ K, $A_f = 254$ K. Generally speaking, $T_0(0)$ can be expressed as $T_0(0) = (1/2)(M_s + A_f)$. So $T_0(0)$ is 225 K. The transformation

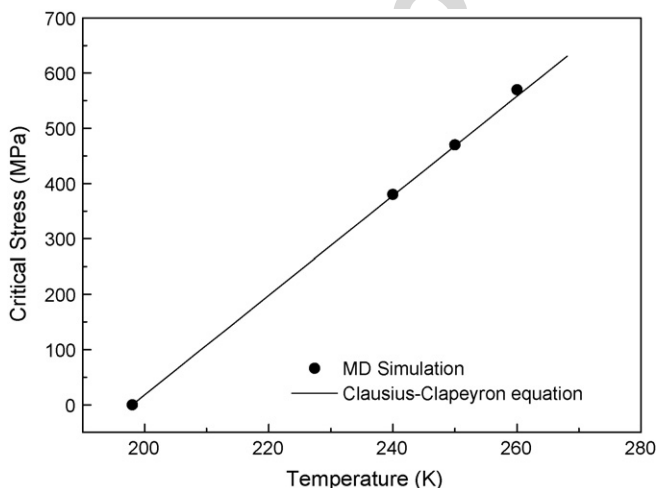


Fig. 4. Comparison between MD simulation and Clausius–Clapeyron equation.

strain from B2 to L1 $_0'$ is 2.5%. The enthalpy change of phase transformation can be calculated as $\Delta H = \Delta U + P\Delta V$, where P is the atmospheric pressure, ΔU and ΔV are the changes of internal energy and volume per mole of the phase transformation, respectively, which are 399.36 J/mol and 1.99 mm 3 /mol, respectively, in the present ensemble. Furthermore, the equivalent atomic weight of Ti–Ni is 53.3 g/mol, and its equivalent density is 6.73 g/cm 3 . Based on the above data, ΔH_V of B2 to L1 $_0'$ phase transformation in TiNi can be obtained as -50.33 J/cm 3 .

By substituting the above constants into Eq. (7), the predicted $\sigma_s \sim T$ curve is shown in Fig. 4. It can be seen that the MD result is in good agreement with Eq. (7). The critical stress for stress-induced martensitic transformation increases linearly with the increasing temperature for cubic crystal, and obeys the Clausius–Clapeyron relationship. This also supports the present MD simulation.

5. Conclusion

- (i) After introducing an appropriate atomic potential into Material Explorer2.0, we simulated for the first time the superelasticity of the shape memory alloys by using molecular dynamics method.
- (ii) A new method for calculating the elastic constant C' is proposed, and then the variation of C' in SIM is simulated. It is found that elastic constant softening is a common feature both in temperature-induced and stress-induced martensitic transformation.
- (iii) Elastic constant C' decreases gradually with increasing external stress prior to SIM. The critical stress σ_s increases linearly with the increasing temperature, following the Clausius–Clapeyron relationship.

Acknowledgements

The authors graciously acknowledge the support of National Science Foundation of China, a special fund for Cheungkong professorship as well as National Basic Research Program of China under Grant No. 2004CB619303.

References

- [1] K. Otsuka, X. Ren, Prog. Mater. Sci. 52 (2005) 511–678.
- [2] A. Planes, L. Manosa, Solid State Phys. 55 (2001) 159–267.
- [3] P. Moine, J. Allain, B. Renker, J. Phys F: Met. Phys. 14 (1984) 2517–2523.
- [4] X. Ren, K. Taniwaki, K. Otsuka, T. Suzuki, K. Tanaki, Y.I. Chumlyakov, T. Ueiki, Phil. Mag. A 75 (1999) 31–41.
- [5] X. Ren, N. Miura, K. Otsuka, T. Suzuki, K. Tanaki, Y.I. Chumlyakov, Mater. Sci. Eng. A 190 (1999) 273–275.
- [6] X. Ren, N. Miura, J. Zhang, K. Otsuka, K. Tanaka, M. Koiwa, Mater. Sci. Eng. A 312 (2001) 196–206.
- [7] D. Shindo, Y. Murakami, T. Ohba, MRS Bull. 27 (2002) 121–127.
- [8] S.M. Shapiro, E.C. Svensson, C. Vettier, B. Hennion, Phys. Rev. B 48 (1993) 13223–13229.
- [9] T. Ohba, S.M. Shapiro, S. Aoki, K. Otsuka, Jpn. J. Appl. Phys. 33 (1994) L1631–L1633.
- [10] L. Manosa, A. Gonzalez-Comas, E. Obrado, A. Planes, V.A. Chernenko, V.V. Kokorin, E. Cesari, Phys. Rev. B 55 (1997) 11068–11071.

- [11] M. Stipcich, L. Manosa, A. Planes, *Phys. Rev. B* 70 (2004) 054115.
- [12] T. Suzuki, M. Shimono, *Phys. Rev. Lett.* 82 (1999) 1474–1477.
- [13] T. Suzuki, M. Shimono, X. Ren, M. Wuttig, *J. Alloy Compd.* 355 (2003) 183–187.
- [14] S. Kazanc, S. Ozgen, O. Adiguzel, *Phys. B* 334 (2003) 375–381.
- [15] M. Parrinello, A. Rahman, *J. Appl. Phys.* 52 (1981) 7182–7190.
- [16] T. Suzuki, M. Shimono, *J. Phys. IV (France)* 112 (2003) 129–132.
- [17] C.M. Wayman, K. Otsuka (Eds.), *Shape Memory Materials*, Cambridge University Press, Cambridge, 1998, pp. 24–25.

Author's personal copy