Journal of the Mechanics and Physics of Solids 61 (2013) 2522–2536

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Entropic stabilization of austenite in shape memory alloys

Ryan S. Elliott*, Daniel S. Karls

Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455, USA

ARTICLE INFO

Article history:
Received 19 February 2009
Received in revised form
24 July 2013
Accepted 30 July 2013
Available online 9 August 2013

Keywords:
Entropic stabilization
Phase transformation
Vibrations
Constitutive behavior
Stability and bifurcation

ABSTRACT

Martensitic transformations (MTs) are the key phenomena responsible for the remarkable properties of Shape Memory Alloys (SMAs). Recent Density Functional Theory (DFT) electronic structure calculations have revealed that the austenite structure of many SMAs is a saddle-point of the material's potential energy landscape. Correspondingly, the austenite is unstable and thus unobservable at zero temperature. Thus, the observable high temperature austenite structure in many SMAs is *entropically stabilized* by nonlinear dynamic effects.

This paper discusses the phenomenon of entropic stabilization of the austenite phase in SMAs and explicitly demonstrates it using Molecular Dynamics (MD) and a *three-dimensional all-atom* potential energy model whose equilibria crystal structures correspond to commonly observed SMA phases. A new technique is used to carefully select a model so that it is likely to lead to entropic stabilization of a B2 cubic austenite from a B19 orthorhombic martensite. This is accomplished by using a detailed branch-following and bifurcation (BFB) parametric study of the Morse pair potential binary alloy model. The results of the MD simulation clearly demonstrate the entropic stabilization of the B2 austenite phase at high temperature. Analysis of the dynamics of the B2 austenite phase indicates that its stabilization may be viewed as a result of *individual* atoms randomly visiting the B19 and αIrV phases (with only occasional visits to the B2 and $L1_0$ phases). This occurs without long-range correlations in such a way that each atom's time-average configuration corresponds to the B2 structure.

1. Overview of phase transformation in shape memory alloys

The Martensitic transformation (MT) has long been identified as the mechanism responsible for the most conspicuous properties of shape memory alloys (SMAs): the shape memory effect and pseudoelasticity. These transformations involve a coordinated rearrangement of atoms in the crystalline material that results in a transition from the austenite phase, a high symmetry high temperature crystal structure, to the martensite phase, a lower symmetry low temperature crystal structure. The ability to quantitatively predict and even design the behavior of SMAs is important because of the current technological prevalence and future prospects of SMAs in fields ranging from civil infrastructure construction to the aerospace industry to biomedical applications. A detailed picture of the MT process at the atomic scale is critical for developing the ability to model and design new SMAs with optimal material properties. In particular, the development of accurate atomistic-based multiscale models of SMAs will be a key to the successful prediction of macroscopic SMA behavior.

At the single crystal scale, continuum mechanics based energy minimization methods have been used to justify the observed complex laminar and needle-like microstructures that are the hallmark of MTs (James, 1986; Ball and James, 1987; Patoor et al., 1988, 1993; James et al., 1995; Shield, 1995; Goo and Lexcellent, 1997; Huang and Brinson, 1998; Vivet and Lexcellent, 1998; James and Hane, 2000; Guthikonda et al., 2008; Beatty and Hayes, 2005). Further, these methods have been very successful in quantitatively predicting many of the properties of these microstructures. These methods are based on a model of the SMA's free energy that includes the existence of multiple "energy wells." At low temperature, the

* Corresponding author. Tel.: +1 612 624 2376.
E-mail address: elliott@aem.umn.edu (R.S. Elliott).

0022-5096/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jmps.2013.07.013

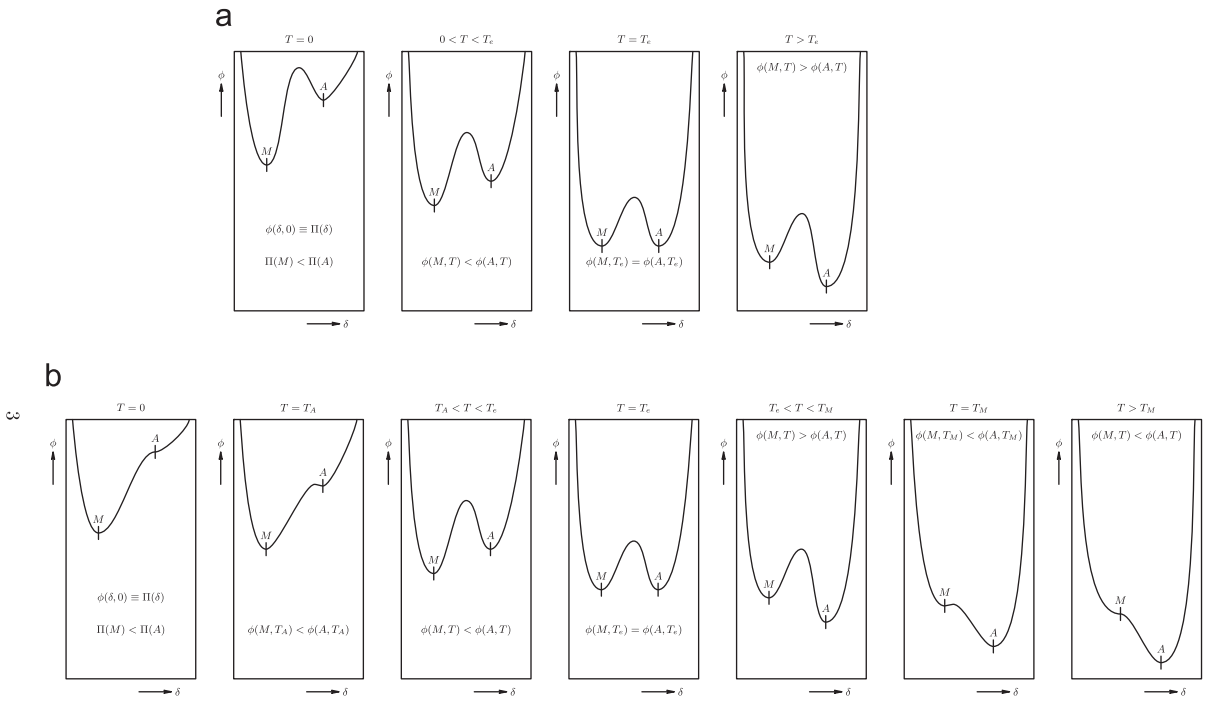

Fig. 1. Two possible schematic representations of the specific free energy $\phi(\delta,T)$ as a function of a controllable deformation δ and the temperature T for a typical SMA. At T=0 K the free energy reduces to the potential energy density $\Pi(\delta)$. (a) Schematic representation of the specific free energy $\phi(\delta,T)$ suggested by many continuum-based SMA models. The equilibrium transition temperature T_e is defined as the temperature at which the free energy of austenite is equal to that of martensite. (b) Schematic representation of the specific free energy $\phi(\delta,T)$ suggested by recent first principles models. The "austenite start" temperature T_A and "martensite finish" temperature T_M are defined as the temperature at which the austenite and martensite phases transition from a local energy minimum to a local saddle point, respectively.

(symmetry related) martensite wells have lower free energy than the austenite well. As the temperature is increased, the energy levels of the martensite and austenite wells move closer together. At the equilibrium temperature T_e they are equal and for temperatures exceeding T_e the austenite well has the lowest free energy (see Fig. 1a).

Strictly speaking, these continuum models are designed for use within a small range of temperature and mechanical loading conditions centered about the transition point. However, it is easy (especially for students) to lose sight of this fact and to expect the austenite and martensite phases to correspond to local energy minimizers of the *potential energy* (at zero temperature). A continuum model based on this assumption would be designed to have the character shown schematically in Fig. 1a. It would then be natural to expect that the potential energy obtained from an appropriate *atomistic* model would have a similar form. However, it is now clear, at least for a representative set of SMAs, that this is incorrect.

Recent first principles calculations of SMAs (Ye et al., 1997; Huang et al., 2002; Parlinski and Parlinska-Wojtan, 2002; Parlinski et al., 2003) have revealed a different picture of the potential energy landscape. These investigations have shown that at zero temperature the austenite phase does not correspond to a local energy minimum, but rather to a saddle point. Thus, a more correct depiction of the free energy landscape of an SMA would be like that shown in Fig. 1b. Here, the martensite phase is a local minimum with low energy at zero temperature while the austenite phase is an unstable equilibrium state and is thus unobservable. At T_A the austenite phase becomes a shallow local minimum but still has high energy when compared to the martensite phase. Between T_A and T_e the austenite phase becomes a deeper local minimum until it reaches an energy level that is equal to the martensite value. Above T_e the austenite well has lowest energy and the martensite well becomes a shallow minimum. Eventually, at T_M, the martensite phase ceases to correspond to an observable local minimum of the free energy.

The phenomenon associated with the transition of a saddle point in the potential energy into a local minimum in the free energy is known by many names including entropic stabilization, soft (phonon) mode theory, and thermal stabilization (see, for example, Dove, 1993; Etxebarria et al., 1992; Kastner, 2006).[1] This is the result of nonlinear dynamic effects of the atomic vibrations in the bulk crystal. For temperatures above T_A, the atomic vibrations (or "phonons") are capable of taking up small oscillations about the potential energy saddle point, resulting in the possibility of observation of the austenite phase. Above T_e the specific entropy s associated with these oscillations becomes large enough to make austenite the thermodynamically stable phase with the lowest free energy.

[1] It is possible, in principal, for dynamical systems to oscillate about an average configuration that corresponds to a local maximum or even a generic point on the potential energy landscape. However, the high degree of symmetry found in crystalline materials makes a saddle point the *most likely* type of configuration for which such an entropic stabilization will occur.