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Martensite modulus dilemma in monoclinic NiTi-theory and experiments

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ABSTRACT

Correct assessment of the NiTi martensite moduli and its significance are the subject of this paper. Current experiments and published experimental data reveal the considerable difference between the macroscopic elastic moduli for twinned martensite and detwinned martensite (single crystal state). Although this difference is significant, it is not explained adequately, and often neglected in modeling. In this study, based on the atomistic simulations, we establish Voigt and Reuss bounds and Hill's estimate for macroscopic moduli for both the internally twinned states and single crystal (detwinned) states. The predicted elastic moduli in the twinned state compare favorably to the experimental thermally induced martensite (with internal twin arrangement) moduli. The single crystal moduli predictions conform to the experimental moduli for deformed martensite or stress-induced martensite in tension and compression showing asymmetry. We draw attention to the need for correct interpretation of the elastic moduli for understanding a wide range of phenomena in shape memory alloys, such as the transformation stress–strain response, the fatigue behavior, the stored elastic energy, the stress hysteresis and others.

1. Introduction

Due to the technological significance of NiTi shape memory alloys (SMAs) (Funakubo, 1987; Otsuka and Wayman, 1998), the knowledge of the elastic moduli of NiTi martensite is essential (Liu and Xiang, 1998; Sehitoglu et al., 2002), yet not well understood. The SMA's thermoelastic martensitic transformation depends on the stored elastic energy Ezaz et al., 2011; Wagner and Windl, 2008), which is a function of martensite elastic moduli. The mechanical response of SMAs, especially in the martensitic state, is rather complex because the martensite morphology undergoes a transition from a multi-variant ('internally twinned') state to a single variant (''detwinned'') arrangement (Liu et al., 1999; Sehitoglu et al., 2003). As transition occurs from a multi-variant twinned morphology to a single crystal one, the accompanying elastic moduli increase can be nearly a factor of three (from 50 GPa to 130 GPa in tension in NiTi). Furthermore, the martensite in binary NiTi has a monoclinic crystal structure with 13 constants (Hatcher et al., 2009; Wagner and Windl, 2008). Thus, phenomenological modeling efforts utilizing lower number of constants (ignoring the anisotropy) or same modulus for martensite relative to austenite may not conform to experiments (Auricchio et al., 1997; Liang and Rogers, 1990; Tanaka, 1986). Overall, there is an incomplete understanding of the elastic modulus in martensitic SMAs (Lagoudas, 2010). This is borne out by recent experimental efforts (Benafan et al., 2012; Šittner et al., 2013; Rajagopalan et al., 2005; Stebner et al., 2013) that have vigorously interrogated the 'overall' elastic moduli in NiTi utilizing various techniques, including high energy diffraction.

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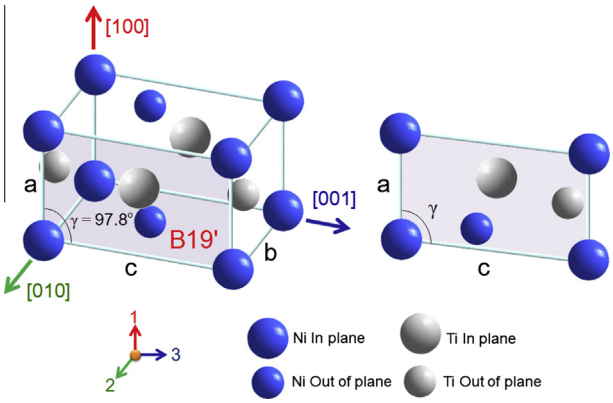

Fig. 1. Crystal structure of martensite B19′ NiTi. Lattice parameters *a*, *b*, and *c* and monoclinic angle γ are marked. The blue and grey atoms represent Ni and Ti, respectively. The different size of atoms indicates atoms are in plane and out of plane. The Cartesian 1- and 2-directions are along with lattice vectors *a* and *b*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Yet, a clear comparison of the 13 moduli terms between martensite 'single crystals' and 'internally twinned' martensite is desired and can be obtained from 'ab initio' studies. This paper addresses this need. In particular, the shear modulus determination on the (001) twin plane is of utmost significance, it will be shown in this study that its magnitude is four times smaller for 'internally twinned' states compared to the 'single' crystal states.

The elastic moduli of martensite can be determined experimentally either below the martensite finish temperature, or during pseudoelasticity upon austenite to martensite transformation. In both cases, the elastic loading or unloading of the stress–strain curves has been extensively utilized in past studies. In the first case, the measured modulus in the martensitic regime under small (initial) deformations was found to be rather low (<50 GPa, also reported later in the paper). This led to many reports where elastic modulus of martensite was tabulated at a lower value than austenite (Hodgson et al., 1990; Duerig et al., 1990). On the other hand, the modulus of martensite after transformation or martensite deformed to high strains has been measured as rather high (>100 GPa), in fact higher than austenite modulus (Sehitoglu et al., 2000). The question then arises, what is the source of this difference?

We offer a simple explanation on this perplexing evolution in 'stress-induced' martensite elastic moduli. We use the term 'stress-induced' because of the evolving magnitude of the elastic moduli as the martensite detwins. When the SMA is cooled below martensite finish temperature under zero external stress, a self-accommodating martensite morphology develops (Otsuka and Wayman, 1998). This martensite morphology is internally twinned (Wechsler et al., 1953) and is referred to as 'thermal martensite'. When deformed in the martensitic regime, the stress–strain response is governed by the growth of preferred variants with respect to others (Duerig et al., 1990). An effective or apparent moduli, representing the detwinning of the variants, are measured. Specifically, when deformed to large strains in tension, the martensite elastic modulus will ultimately represent the displacement of atoms in '*c*' direction which is the largest lattice constant (see Fig. 1). This means that under tension loading the martensite with the longest lattice axis (termed [001] in this study) vertical is preferred. Upon application of compression, the preferred direction is [100] with the shortest lattice axis or the '*a*' axis being vertical. So, the effective modulus observed depends on the orientation (texture) of the crystal, and can exhibit tension–compression asymmetry.

The DFT (density functional theory) calculations for elastic moduli along lattice vectors should agree with the loading–unloading measurements after high strains in tension and compression. We show experimental results that conform to the statement above on laboratory samples without grain boundaries. On the other hand, these DFT calculations for single crystals cannot be directly used to establish the macroscopic moduli of the twinned structure (the initial moduli of the martensite). This paper forwards a 'twinned' crystal unit cell for modeling the twinned martensite moduli. So what should one use in mechanics (continuum or crystal level) simulations of the martensite response? To assign a constant value for martensite modulus would be deficient. This is borne out by experiment. We conduct DFT calculations and illustrate how the modulus of a 'twinned structure' can be calculated and subsequently obtain the macroscopic moduli. Also, as stated earlier we reveal a direct comparison between the shear moduli calculation based on the 'twinned state' compliance tensor and the shearing moduli from the Generalized Planar Fault Energy (GPFE) curve with very good agreement.

2. Elastic constants of B19′ NiTi

The martensitic NiTi has a B19′ monoclinic crystal structure with lattice parameters a = 2.88 Å, b = 4.11 Å, c = 4.66 Å and a monoclinic angle γ = 97.8° (Fig. 1). These parameters, determined from structural energy minimization in our previous DFT calculations (Ezaz et al., 2011), will be used in the present study. Here, the monoclinic angle γ is between the [100] and [001] directions. The *c*-axis is the longest axis and the *a*-axis is the shortest one, while the *b*-axis is the intermediate (we