

An *in situ* neutron diffraction mechanical study of superelastic NiTi and NiTi-TiC composites

R. Vaidyanathan, M.A.M. Bourke¹ and D.C. Dunand²

AMPAC and MMAE, University of Central Florida, Orlando, FL 32816-2455, U.S.A.

¹ MST-8, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.

² Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, U.S.A.

Abstract Superelastic NiTi and NiTi-TiC composites were subjected to static uniaxial compressive loading while neutron diffraction spectra were simultaneously acquired. A methodology was established to obtain quantitative strain, texture and phase volume fraction information during the forward and reverse stress-induced martensitic transformation. Despite the presence of 10 vol.% of stiff TiC particles, a macroscopic compressive strain of 3% was obtained in the composite on loading and was fully recovered on unloading. The observed behavior suggests that the martensite accommodates the mismatch with the transforming austenite (while they co-exist) and the TiC particles (in the case of the composite). Superelastic NiTi was also subjected to simultaneous neutron diffraction and uniaxial compressive cycling. The average phase strain in the mechanically-loaded austenite (at a given stress) remained unaltered during the load-unload cycles. However, differences in both volume fraction and texture of austenite and martensite were noted as cycling progressed, suggesting that these factors are responsible for the changes in the macroscopic stress-strain response of NiTi with mechanical cycling.

1. INTRODUCTION

When NiTi is mechanically loaded, a stress-induced austenitic to martensitic phase transformation can result in macroscopic strains as high as 8%. On unloading, the martensite becomes unstable and transforms back to austenite, with a concomitant macroscopic strain recovery. This phenomenon is called the superelastic or pseudoelastic effect and finds application in, e.g., mobile phone antennae, cardiovascular stents and guidewires [1]. By recording diffraction spectra during external loading, this reversible stress-induced austenite to martensite transformation can be investigated *in situ*. Such data can provide quantitative phase-specific information on the elastic strain, texture and phase volume fraction evolution. The basic principle of such measurements for strain determination involves using the lattice plane spacing of grains as internal strain gauges. For texture, the relative intensities of the peaks are considered and for phase volume fraction, an integrated intensity of peaks corresponding to a specific phase are used.

We summarize and synthesize here a systematic study [2,3] of superelastic NiTi subjected to monotonic and cyclic loading and NiTi-TiC subjected to monotonic, quasi-static loading, while neutron diffraction spectra are simultaneously acquired. The advantage of using neutrons over conventionally produced x-rays is that the bulk behavior can be investigated in polycrystalline samples (the 50% transmission thickness in NiTi for Cu-K_α x-rays is approximately 9 μm as compared to about 3 cm for thermal neutrons) [4]. The spectra were recorded while interrupting the cycle (but continuing to apply a constant load) during loading and unloading portions of the stress-strain curve. The diffraction experiments allowed for a comparison between the microstructural texture, phase volume fraction and strain changes during the stress-induced austenite to martensite transformation and the macroscopic stress-strain response.

2. EXPERIMENTAL

Information on the experimental setup can be found elsewhere (e.g., [5,6]) and is only summarized here. Neutron diffraction measurements were performed in ‘time of flight’ mode using the Neutron Powder Diffractometer (NPD) at the pulsed neutron source at Los Alamos National Laboratory (LANL) as schematically illustrated in Figure 1a. Three series of experiments [2,3] on hot isostatically processed (HIPed) samples were performed:

(a) Uniaxial compressive loading of NiTi up to 975 MP and subsequent unloading (see Figure 1b);

(b) Cyclic compressive loading and unloading (100 cycles) of NiTi up to 975 MPa (see Figure 1c);
 (c) Uniaxial compressive loading of NiTi-TiC up to 975 MP and subsequent unloading (see Figure 1b).
 Samples were loaded in compression while neutron diffraction spectra were simultaneously acquired at three scattering angles. The loading axis formed an angle of 45° with the incident polychromatic neutron beam, allowing measurements for which the scattering vector was parallel and perpendicular to the loading axis. A third detector was used in back-scattering geometry. An extensometer was attached to the samples to record macroscopic strain during the experiments.

3. NEUTRON DIFFRACTION SPECTRA ANALYSIS

The Rietveld refinement technique, implemented in the LANL code General Structure Analysis System (GSAS) [7], was used to analyze the neutron diffraction spectra. In the Rietveld method, intensity at every point in the spectrum was determined by adding the calculated background and Bragg scattering intensities corresponding to diffraction peaks. The refinement procedure varied selected parameters (e.g. phase volume fractions, atom positions and phase texture) until the calculated and measured spectra matched in a least squares fit. Errors associated with the statistics of the fit were quantified. In particular, the procedure incorporated changes in diffraction peak intensities due to texture. A generalized spherical harmonic description was used to account for the evolving texture in the austenite and martensite phases. The profile function which fitted the data best was a combination of two functions: the first was the result of convoluting two back-to-back exponentials with a Gaussian and the other was a linear combination of a Lorentzian and a Gaussian (pseudo-Voigt).

For the austenite and TiC phases, two formulations of the strain were used [8]. In the first approach, the refinement procedure determined a lattice parameter by fitting many individual reflections. The elastic lattice strain was then reported as

$$\begin{aligned}\varepsilon_{\text{aus}} &= \frac{a_s^{\text{aus}} - a_o^{\text{aus}}}{a_o^{\text{aus}}} \\ \varepsilon_{\text{TiC}} &= \frac{a_s^{\text{TiC}} - a_o^{\text{TiC}}}{a_o^{\text{TiC}}}\end{aligned}\quad \dots 1$$

where a_s was the austenite or TiC lattice parameters under an applied compressive stress and a_o was the respective lattice parameters under no external load. A compressive stress of 8 MPa was used to hold the sample horizontally in the stress rig and corresponds to this 'no load' condition. In Eq. 1, no attempt was made to accommodate the lattice plane (hkl) specific anisotropy and the implicit assumption is made that either the strain has no lattice plane dependence or is a reasonable average over all lattice planes.

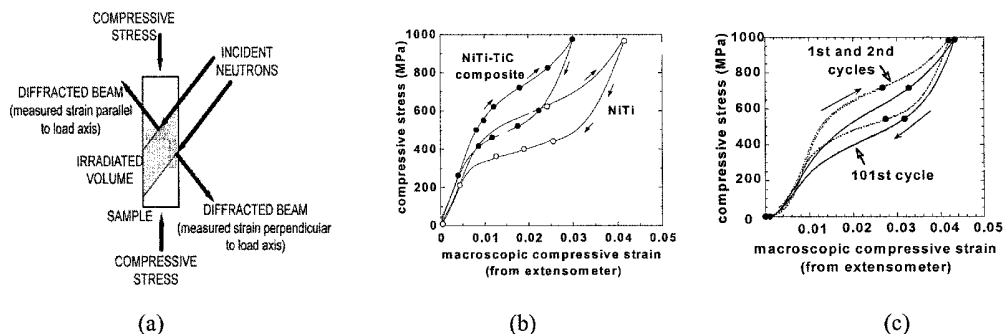
In the second approach, a strain anisotropy term was incorporated in the Rietveld procedure and the strain was reported for a specific plane as a contribution of isotropic (hkl-independent) and anisotropic (hkl-dependent) components:

$$\begin{aligned}\varepsilon_{\text{aus}}^{\text{hkl}} &= \varepsilon_{\text{aus}}^{\text{iso}} - A_{\text{hkl}} \varepsilon_{\text{aus}}^{\text{aniso}} \\ \varepsilon_{\text{TiC}}^{\text{hkl}} &= \varepsilon_{\text{TiC}}^{\text{iso}} - A_{\text{hkl}} \varepsilon_{\text{TiC}}^{\text{aniso}}\end{aligned}\quad \dots 2$$

where $A_{\text{hkl}} = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2$. The isotropic strain component, ε^{iso} , was determined by shifting individual lattice reflections so as to account for a change in the lattice parameter, as in Eq. 1. The anisotropic strain component, $\varepsilon^{\text{aniso}}$, further shifts individual reflections proportional to A_{hkl} . The A_{hkl} dependence was introduced because in a cubic single crystal the plane specific modulus, E_{hkl} , can be expressed as

$$\frac{1}{E_{\text{hkl}}} = S_{11} - 2(S_{11} - S_{12} - \frac{S_{44}}{2})A_{\text{hkl}}\quad \dots 3$$

where S_{ij} is the single crystal compliance tensor in collapsed matrix notation. The A_{hkl} dependence was originally formulated to capture the elastic anisotropy in single crystals and was used here since it *empirically* captures the elastic anisotropy in polycrystals and the anisotropy introduced by the austenite to martensite transformation in polycrystalline NiTi.



(a) Schematic of the experimental set-up at Los Alamos National Laboratory showing the incident beam and two of the three diffracted beams with respect to the loading direction. The irradiated volume is about 1 cm³. Representative macroscopic compressive stress-strain responses of (b) superelastic NiTi and NiTi-TiC during loading and unloading and (c) cyclic loading of superelastic NiTi samples, which were tested in the neutron beam. The symbols on the curves indicate the stresses at which loading was interrupted and neutron diffraction spectra recorded.

4. RESULTS AND DISCUSSION

4.1 Uniaxial loading-unloading of NiTi and NiTi-TiC (Ref. [2])

4.1.1 Phase volume fraction evolution

The generalized spherical harmonic texture formulation in Rietveld refinements provided a determination of austenite and martensite phase volume fractions coexisting under an applied stress in NiTi and NiTi-TiC. A linear relationship was observed between the volume of stress-induced martensite and the macroscopic strain generated by the transformation for both NiTi and NiTi-TiC. The volume fraction of martensite formed at any given applied stress and the recoverable strain decreased in the presence of TiC particles. This is understandable given that the most favorable variant, in terms of the macroscopic strain, may not be compatible with a non-transforming TiC particle in its proximity and may thus not form.

4.1.2 Texture evolution

In NiTi and NiTi-TiC, the overall texture of the martensite decreased with increasing stress. This was attributed to favorable orientations of austenite transforming first to martensite and the need for the later-forming martensite to be compatible with the already transformed martensite (and TiC). On comparing the texture of martensite formed in the presence and absence of TiC at the same superelastic strain, it was observed that martensite in the presence of TiC was less textured. This is understandable since there are more spatial constraints for the formation of martensite when TiC is present. This situation is analogous to martensite forming at lower strains (where fewer constraints exist) being more textured than the martensite forming at higher stresses (where other martensite plates preclude certain orientations).

4.1.3. Strain evolution

Significant discrepancies were observed between the Young's moduli for NiTi and NiTi-TiC measured by extensometry and predicted using single crystal data and Eshelby theory. The differences were attributed to small amounts of austenite transforming to martensite at low stresses, which reduce the apparent moduli. In contrast to the macroscopic data, the modulus of austenite in NiTi measured by neutron diffraction (from the slope of applied stress vs. elastic strain response) compared well with moduli predicted using single crystal data (Hashin-Shtrikman bounds and Hill average). The applied stress at which austenite transforms to martensite and back to austenite increased in the presence of TiC particles. For both NiTi and NiTi-TiC, the elastic lattice strain in the austenite remained linear with respect to the applied stress even when significant volume fractions of austenite had transformed to martensite, but

showed some non-linearity at higher applied stress. This load transfer coupled with the stress hysteresis results in strains in the austenite during unloading being somewhat larger than strains during loading, for the same stress. For the composite, good agreement was observed in the phase strains predicted by Eshelby elastic theory and measured by neutron diffraction. In general, the self-accommodating nature of the stress-induced martensite almost eliminated the mismatch with the TiC particles and the transforming austenite. Additional anisotropy introduced by strain redistribution due to the transformation was reflected in changes in the anisotropic component of the strain of the austenite phase in NiTi-TiC.

4.2. Cyclic loading (Ref. [3])

The change in macroscopic stress-strain behavior at intermediate stresses where martensite and austenite coexist was found to result from an increase in both volume fraction and texture in the stress-induced martensite. The average elastic strain in austenite remained mostly unchanged at intermediate stresses, but the isotropic and anisotropic components of the strain in austenite redistributed themselves. The residual elastic strain present after unloading in austenite also evolved during cycling. These phenomenological observations shed light on the materials evolution occurring during repeated reversible stress-induced transformation in superelastic NiTi, of importance both during mechanical training of NiTi devices and during their subsequent use.

5. SUMMARY

We summarize here a systematic study of the microstructural and micromechanical changes responsible for the macroscopic stress-strain curve in NiTi and NiTi-TiC composites, using *in situ* neutron diffraction measurements [2,3]. Despite the presence of 10 vol.% of stiff TiC particles, a macroscopic strain of 3% was obtained in the composite on loading and was fully recovered on unloading.

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