Deformation behavior of Nb nanowires in TiNiCu shape memory alloy matrix

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Abstract: An in-situ nanowire Nb/TiNiCu composite is fabricated based on the concept of strain under-matching between a phase transforming matrix and high strength nanomaterials. The deformation behavior of the Nb nanowire was investigated by means of in-situ synchrotron X-ray diffraction when the TiNiCu matrix underwent different deformation modes. The maximum lattice strain of the Nb nanowires was about 5% when the matrix deformed via martensitic transformation or 1% when deforming plastically by dislocation slip. The Nb nanowires showed a lattice strain of 3.5% when the matrix deformed in the mixed mode of plastic deformation and martensitic transformation, which means that the occurrence of plastic deformation does not impede load transfer from the matrix to the nanowires.

Keywords: Shape-memory alloy; TiNiCu; Martensitic transformation; Composite; Nanowire; Synchrotron x-ray diffraction;

1. Introduction

Nanomaterials, such as nanowires, nanotubes and nanoribbons, are known to exhibit exceptional mechanical properties approaching theoretical limits [1]. Owing to this, much effort has been made in the past to develop nanomaterials-reinforced composites to harness their exceptional properties in bulk forms. However, results obtained so far are disappointing [2]. Recently, this situation has been broken through by a new design concept of strain matching between a phase transforming matrix and high strength nanomaterials [3], and was further verified by other nanocomposites showing superior properties [4, 5]. This strain matching mechanism allows effective load transfer between the two components [6, 7], leading to achievements of the extremely large elastic strains in the nanomaterials and remarkable high performance of the composite [3-5].

It should be noted that during the firstly proposed concept of strain matching, it mentioned only an approximate match in magnitude of the lattice strains between the martensitic transformation of the matrix and the elastic deformation of the nanowires [3]. Actually, in that work the B2-B19' transformation strain of TiNi (~7%) over-matches the

elastic strain limit (4.2%~6.5%) of the Nb nanowires [1]. As we know, there are lots of martensitic transformations whose transformation strains are less than 7%. One of them is the B2-B19 transformation in the TiNiCu shape memory alloys with a lattice strain of about 3% [8-10], which is less than half of the lattice strain of the B2-B19' transformation in TiNi and significantly below the expected elastic strain limit of Nb nanowires (~6.5% [3]). Thus, if the nanowires are embedded in this kind of matrix, will the lattice strain of the nanowire be limited by this strain under-matching? In this work, we investigated an opposite scenario of over-matching, where the martensitic transformation strain of the matrix under-matches the elastic strain limit of the nanowire.

It has been pointed out that the strain matching mechanism requires that the matrix deforms by uniform lattice distortion via its martensitic transformation, as opposed to plastic deformation via dislocation slip [3], to be effective for load transfer from the matrix to the nanowires. In this regard, it is also of interest to investigate the deformation behavior of the nanowires when the matrix deforming by a mixed deformation modes of the martensitic transformation and plastic deformation in addition to their single deformation mode. This can be achieved by choosing the temperature at which the tensile test is performed [11].

2. Experimental procedure

An ingot of 0.5 kg with composition of $(\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10})_{93}\text{Nb}_7$ was produced from high-purity elemental metals of the constituents (purity >99.8 wt. %) by arc melting. The ingot was hot-forged at 800 °C and further hot-drawn at 500 °C into a thick wire of 2 mm in diameter. The hot-drawn wire was then cold-drawn into a thin wire of 0.5 mm in diameter at room temperature with intermediate annealing at 630 °C. Samples were cut from the cold-drawn wire and then annealed at 400 °C for 20 min or at 600 °C for 20 min followed by air cooling. A FEI Quanta 200F scanning electron microscope (SEM) and a Tecnai F20 transmission electron microscope (TEM) were used for microstructure characterization. In-situ synchrotron high energy X-ray diffraction (HEXRD) measurements were performed to study the deformation behavior of the phase constituents of the composite wire, and the experiment was conducted at the 11-ID-C beamline of the Advanced Photon Source at Argonne National Laboratory. High-energy X-ray with a beam size of 0.4 mm×0.4 mm and wavelength of 0.010798 nm was used to obtain two-dimensional (2D) diffraction patterns in the transmission geometry.

3. Results and discussion

Fig. 1 shows typical microstructure of the composite wire. As seen in Fig. 1(a), the alloy has a hypo-eutectic microstructure, consisting of primary dendrites (gray area) and an ultra-fine eutectic lamellar structure (bright area). The inset in Fig. 1(a) shows the eutectic lamellar structure at a higher magnification. The bright area is a Nb-rich phase and the dark area is TiNiCu, as confirmed by EDS analysis. This microstructure is similar to our previous report with Nb-rich phase and TiNiCu matrix [12]. This is further evidenced by the elemental mapping analysis of the composite wire (Fig. 1(d)). Cu is found to be dissolved in the TiNi phase and not in the Nb-rich phase. The volume fraction of Nb nanowires is about 10%.

Fig. 1. Microstructure of the composite. (a) SEM back scattered electron micrograph of the ingot. The inset is a high magnification SEM image showing details of the eutectic structure. (b) TEM bright field image of the composite wire in the longitudinal direction. (c) High energy X-ray diffraction pattern of the composite wire. (d) STEM-HAADF image and EDS elemental mapping of the composite wire.

Fig. 1(b) is a TEM bright field image of the cold-drawn composite wire, revealing that the in-situ formed Nb nanowires have a mean diameter of 60 nm and are well dispersed and aligned in the TiNiCu matrix along the wire axial direction. The Nb fine lamellae in the eutectic area were converted into Nb nanowires via severe deformation during wire drawing of the as-cast TiNiCu-Nb hypo-eutectic alloy. Fig. 1(c) shows the high-energy X-ray diffraction pattern of the composite wire. The diffraction pattern is indexed to bcc-Nb and B2-TiNiCu phases. The HE-XRD pattern also demonstrates that the Nb nanowires have a strong [110] texture along the wire axial direction.

Fig. 2 shows the tensile stress-strain curves of the three composite wire samples, which were heat treated under different conditions and tested at room temperature (RT) and 200 °C. All three samples showed similar yield strength of about 600 MPa, but with quite different work-hardening behavior thereafter. S1 showed strongest work-hardening and reached an ultimate strength of 1.77 GPa and an elongation of 14%. S2 also showed a significant work-hardening behavior and reached an ultimate strength of 1.44 GPa and elongation of 9%. No work-hardening was observed for S3, which showed an ultimate strength of 880 MPa and an elongation of 9%.

Fig. 2. Tensile stress-strain curves of the composite wires. S1: a sample annealed at 400 °C and deformed at the room temperature, S2: a sample annealed at 400 °C and deformed at 200 °C, S3: a sample annealed at 600 °C and deformed at 200 °C.

Fig. 3 shows in-situ synchrotron HEXRD measurements during tensile loading of the three samples. All the diffraction spectra are integrated from the 2D pattern along the axial direction of the samples. For sample S1 (Fig. 3 (a)), the Nb-(110) diffraction peak shifted gradually to higher d -spacing values and then remained unmoved with further deformation at above 10% global strain. The B19-(001) peak emerged at 2.3% global strain (Fig. 3(b)), at which point the B2-(110) diffraction peak disappeared (the blue box in the right lower corner of Fig. 3(a)). This implies the occurrence of the stress induced martensitic transformation (SIMT) at the point of deformation corresponding to “A” as marked on the stress-strain curve in Fig. 2. The B19-(001) martensitic peak, once emerged, also shifted gradually to higher d -spacing values with increasing global strain (Fig. 3(b)), implying its elastic deformation.

Fig. 3. Evolution of B2-TiNiCu (110), Nb-(110) and B19-TiNiCu (001) diffraction peaks in the direction perpendicular to the loading direction. (a) and (b): S1. (c) - (e): S2. (f) - (h): S3.

Figs. 3(c)-(e) show the evolutions of B2-(110), Nb-(110) and B19-(001) diffraction peaks of S2 during deformation. In addition to the expansion of the d-spacing along the axial direction, it is also seen that the B19-(001) peak appeared at 5.4% global strain and increased in intensity progressively with continued deformation (the red box in Fig. 3(e)), signifying the gradual occurrence of the B2-B19 martensitic transformation over a wide range of global deformation. It is also evident that the B2-(110) peak did not disappear till the end of the test (rupture), indicating incompleteness of the transformation. The fact that the transformation commenced at such a high level of deformation and over a wide range of global strain implies explicitly that the transformation process was mixed with plastic deformation, apparently due to the strain hardening of the matrix. The starting point of the transformation is indicated on the stress-strain curve in Fig. 2 as “B”.

Figs. 3(f)-(h) show the evolutions of B2-(110), Nb-(110) and B19-(001) diffraction peaks of S3. The B2-(110) peak survived the entire deformation up to 9% of global strain, as for S2, but the B19-(001) peak did not appear (Fig. 3(h)). This implies that the TiNiCu matrix underwent only plastic deformation (and elastic deformation) during loading without SIMT.

Lattice strains in the axial direction are calculated from the diffraction peak positions. Fig. 4 shows the lattice strain measurements for Nb (110) in the loading direction of the three samples as functions of the applied global strain. It is seen that all three samples showed a uniform Nb (110) lattice strain to $\sim 0.8\%$ up to a global strain of 2%. Referring to Fig. 2, it is seen that at this global strain level all three samples showed a similar stress level of 700 MPa. Considering Young's modulus of 85 GPa for B2-NiTiCu [13, 14], an elastic strain of $\sim 0.8\%$ can be expected of the NiTiCu matrix, agreeing well with the magnitude of the uniform elastic strains of the Nb nanowires.

Fig. 4. Evolution of the Nb (110) d -spacing strains in the loading direction with the applied global strain of the three samples.

At above 1.8% global strain, the Nb (110) lattice strains of the three samples departed. S1, which deformed via SIMT in the matrix, showed a sudden jump of 1.2% (A-A') and then continued to increase with further deformation to 4.8% (point C) before apparent yielding thereafter. This total elastic strain is about 1.7% lower than that of the Nb nanowires measured in a TiNi matrix [3]. The strain jump (A-A') corresponds to the sudden appearance of the B19-(001) peak and the disappearance of the B2-(110) peak, as shown in Figs. 3a and 3b, thus is due to the SIMT of the matrix [15-18]. This 1.2% strain jump of the Nb nanowires is about one third of the elastic strain ($\sim 3.8\%$) jump of the Nb nanowires achieved in a TiNi matrix during its B2-B19' transformation [18]. This is apparently related to the small transformation strain of the B2-B19 in TiNiCu. The 2.8% elastic strain of the Nb nanowires after the jump (stage A'-C) is attributed to the continuation of the martensitic transformation as well as the elastic deformation of the stress-induced martensite in the matrix.

The Nb (110) lattice strain of S2, which deformed in a mixed mode of plastic deformation and SIMT, increased continuously with increasing global strain to a maximum of 3.5%. This strain is lower than that achieved in S1, apparently due to the incompleteness of the B2-B19 transformation. This also implies that the occurrence of plastic deformation did not affect the load transfer from the matrix to the Nb nanowire by the martensitic transformation of the matrix (thus the increase of the elastic strain of the Nb nanowires). S3 underwent only plastic deformation. In this case the maximum lattice strain of Nb (110) was only about 1%. This is consistent with our previous study. The intrinsic large elastic strain of the Nb nanowires cannot be achieved in matrices deforming by dislocation slip. This demonstrates the ineffectiveness of load transfer from the matrix to the nanowires during plastic deformation.

Fig. 5 shows comparison of the evolution of lattice strains of both the TiNiCu matrix and the Nb nanowires, for samples S1 and S3. As above, all lattice strains are calculated relative to their initial values. That means the lattice strain of the stress-induced B19 martensite, which appeared at a certain stress level, is underestimated. To compensate for this, the B19(001) strain of sample S1 is tentatively raised so that it coincides with the B2(110) strain at the point of its appearance (apparently under the assumption that the Austenite and the martensite have the same Young's modulus), as indicated by curve B19(001)* in Fig. 5(a).

The difference between the lattice strains of B19(001)* and Nb(110) is apparently due to the lattice distortion of the B2→B19 martensitic transformation. It is apparent that Nb nanowires continued to deform elastically during the stages of elastic deformation and stress induced martensitic transformation of the TiNiCu matrix, until yielding at its elastic limit of $\sim 4.76\%$. After that no further lattice strain was produced in Nb nanowires despite the continued increase of elastic lattice strain of the B19 martensite.

Fig. 5. Evolution of d -spacing strains of the matrix and the Nb nanowires with the applied global strain. (a): S1; (b) S3.

Fig. 5(b) show the comparison of the lattice strains for sample S3, which experienced no stress-induced martensitic transformation. In this case the lattice strains of Nb(110) and B2(110) followed the same trend with similar values. It is evident that the Nb(110) lattice strain stopped increasing rapidly with applied strain at $\sim 1.1\%$, well below its elastic limit. This is apparently limited by the magnitude of the lattice strain of the B2 matrix. The reduced increase of the B2(110) strain at above 2.4% applied strain (or 0.8% lattice strain) is attributed to its plastic deformation.

4. Conclusions

This study investigated the elastic deformation behavior of Nb nanowires in an in-situ nanowire Nb/TiNiCu composite, as an indicator of load transfer from the matrix to the nanowires. The evidence presented above demonstrates that:

- (1) Effective load transfer, thus large elastic strains in the nanowires, is still valid under under-match conditions where the transformation strain of the matrix is smaller than the elastic strain limit of the Nb nanowires.
- (2) The total elastic strain exhibited by the nanowires corresponds to the elastic strain as well as the transformation strain of the matrix. In this case a maximum strain of 4.8% was achieved in the Nb nanowires by the martensitic transformation of the matrix.
- (3) The occurrence of plastic deformation does not impede load transfer from the matrix to the nanowires caused by the martensitic transformation and elastic deformation of the matrix.

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