A biopolymer-like metal enabled hybrid material with exceptional mechanical prowess

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The design principles for naturally occurring biological materials have inspired us to develop next-generation engineering materials with remarkable performance. Nacre, commonly referred to as nature’s armor, is renowned for its unusual combination of strength and toughness. Nature’s wisdom in nacre resides in its elaborate structural design and the judicious placement of a unique organic biopolymer with intelligent deformation features. However, up to now, it is still a challenge to transcribe the biopolymer’s deformation attributes into a stronger substitute in the design of new materials. In this study, we propose a new design strategy that employs shape memory alloy to transcribe the “J-curve” mechanical response and uniform molecular/atomic level deformation of the organic biopolymer in the design of high-performance hybrid materials. This design strategy is verified in a TiNi-Ti3Sn model material system. The model material demonstrates an exceptional combination of mechanical properties that are superior to other high-performance metal-based lamellar composites known to date. Our design strategy creates new opportunities for the development of high-performance bio-inspired materials.

In the game of survival of the fittest, Nature, after millions of years of evolution, presents us with an abundance of rational designs of hierarchically structured materials of exceptional mechanical properties and functionalities that are still beyond the reach of many engineered materials. The design wisdom in these natural materials often inspires us to create and develop new and better man-made materials. Rigid biological materials are renowned for their remarkable mechanical robustness that often far exceeds what can be expected from a simple mixture of their components1−4. One of the best examples is nacre (mother-of-pearl), which is commonly referred to as nature’s armors. Nacre possesses a hierarchical structure of surprising simplicity consisting of brittle inorganic aragonite (a mineral form of CaCO3) platelets sandwiched with soft organic biopolymer layers1−4. The mineral component is in a layered form and serves as the primary load bearer for strength2,3. The soft organic biopolymer layers in-between play a critical role in both load distribution and energy dissipation due to its unique deformation features2,4−6.

Macroscopically, the organic biopolymer responds to external mechanical loading in an intelligent manner (see Table 1 and Fig. 1a). It deforms at a low flow stress up to a large flow strain with a very low hardening effect (or high compliance), followed by a remarkably high strain-stiffening to reach a high ultimate rupture strength4−6. This deformation feature has been referred to as the “J-curve”, in recognition of the shape of the stress-strain (or load-displacement) curve4. The coupling of low flow stress (point A in Fig. 1a) and large flow strain (A–B in Fig. 1a) renders the biopolymer “easy deformability”, acting as a load distributor and deformation coordinator between the brittle mineral and biopolymer components, effectively reducing stress concentration2,5. The strain-stiffening at higher strain levels (B–C in Fig. 1a) effectively prevents excessive local deformation and stable deformation.
“run-away” deformation, thus enabling the composite to achieve a higher ultimate strength. Clearly, the biopolymer component “wisely” manages the deformation in the hierarchical architecture of nacre to prevent/delay catastrophic fracture. Microscopically, the organic biopolymer undergoes these deformation stages through molecular reconfiguration, including uncoiling or straightening (the inset in Fig. 1a), in a uniform manner without introducing discrete structural defects (like dislocations in metals) piling-up at organic-inorganic interfaces. This deformation mode uniformly distributes stress on a molecular/atomic level and expels stress concentration at organic-inorganic interfaces. This deformation mechanism of the organic biopolymer is microscopically favorable for enhancing the toughness and strength of nacre. In this regard, apart from the structural design strategy, the unique “J-curve”-shaped mechanical response and the uniform, rigid-component-friendly molecular/atomic level microscopic deformation feature are two important design criteria in selecting substitute materials for the biopolymer in order to achieve nature’s accomplishments in engineered composites.

Substantial efforts have been devoted to the synthesis of high-performance composite materials by reproducing the hierarchically layered structures of natural rigid biological materials. Several techniques, such as tape or slip casting, layer-by-layer deposition, and freeze casting, have been used to synthesize bio-inspired composite materials. Previously, hard and brittle materials were chosen as the mineral component, whereas synthetic polymers or conventional soft metallic materials were selected as substitutes for the organic biopolymer component. One limitation of using synthetic polymers is their generally low strength, which handicaps the mechanical performance of the composites. The use of metallic materials, which have relatively higher strengths than synthetic polymers, indeed improves the mechanical performance. However, these metallic materials do not exhibit “J-curve” deformation behavior. In addition, they deform by dislocation movement, which is nonuniform at the atomic scale. As a result, conventional metallic materials fail to satisfy either of the two aforementioned design criteria.

A unique and promising choice, which has never been attempted in the past, is shape memory alloys (SMAs). Due to its thermoelastic martensitic transformation, a SMA exhibits...
a “J-curve” stress-strain behavior (Fig. 1c) through a relatively uniform lattice deformation mechanism (the inset in Fig. 1c and Supplementary Fig. 1), which satisfies both design criteria for replicating the organic biopolymer. Upon loading, the SMA experiences a low stress yielding (point A in Fig. 1c) over a large strain (A–B in Fig. 1c) via either a stress-induced martensitic transformation (Supplementary Fig. 1) or martensite variant reorientation by detwinnning (the inset in Fig. 1c). After that, the detwinned martensite rapidly stiffens with increasing strain (B–C in Fig. 1c), which is primarily related to its elastic deformation, to reach a high ultimate strength (point C in Fig. 1c). The second important characteristic of a SMA is the microscopic deformation mechanism. The stress-induced martensitic transformation (Supplementary Fig. 1) or detwinnning of the martensite variants (the inset in Fig. 1a) is a relatively uniform lattice shear distortion with a maximum strain of 10% (in TiNi) and TiNiSn system undergoes a eutectic solidification of TiNi–Ti3Sn to form an in situ submicron laminar composite. In this study, TiNi–Ti3Sn eutectic composite ingots with a chemical composition of Ti57Ni35Sn8 (at. %) were prepared using coupled arc melting and directional solidification techniques. Fig. 2 presents a typical microstructural analysis of the composite. The microstructure consists of fine composite lamellae of TiNi and Ti3Sn (Figs. 2a and 2b) with well-bonded interfaces (Fig. 2c). Selected-area electron diffraction patterns, which were obtained from the bright layer and gray layer (Fig. 2b), confirm the D019-Ti3Sn (Fig. 2d) structure and B19’-TiNi (Fig. 2e) structure, respectively. This observation is consistent with high-energy X-ray diffraction measurements (Fig. 2f). The thicknesses of the TiNi layer and Ti3Sn layer are approximately 300 nm and 200 nm, respectively. The directional solidification process helped to re-arrange the TiNi and Ti3Sn alternating layers in one direction (Supplementary Fig. 2).

To uncover the mechanical response of the TiNi component in the composite, in situ synchrotron high-energy X-ray diffraction (HE-XRD) measurements were performed during compressive deformation (Supplementary Fig. 3). The evolutions of the lattice strains (indicating elastic strains) of TiNi and Ti3Sn in the loading direction as a function of the applied macroscopic strain are shown in Fig. 3a and Supplementary Fig. 4. Fig. 3a illustrates that as the applied strain increased, the lattice strain of TiNi initially increased linearly (O-A), and then remained almost constant at 0.7% to approximately 4% of the applied strain (A–B) before increased rapidly again at higher applied strains (B–C). The TiNi lattice strain reached 1.1% at 9% of applied strain, beyond which the TiNi lattice strain continued to increase at a reduced rate to a maximum of 1.5% (C–D). This mech-
The mechanical response exhibits a "J-shaped" curve between the lattice strain and the applied strain (the inset in Fig. 3a). Considering that the stress endured by the TiNi can be directly converted from its elastic lattice strain via Young’s modulus, the "J-shaped" lattice strain versus the applied strain curve explicitly implies a "J-shaped" stress versus the applied strain curve of the TiNi in the composite. The elastic strain at the yield (point A in Fig. 3a) and the maximum elastic strain (point D in Fig. 3a) of the TiNi component in the composite are 0.15% and 1.5%, respectively. Using $E = 50$ GPa for TiNi, the strengths that correspond to points A and D are estimated to be 75 and 750 MPa, respectively, which are approximately three to 10 times greater than the strengths of the organic biopolymer in natural rigid biological materials.

The microscopic deformation mechanism of the TiNi component during loading was analyzed by in situ synchrotron HE-XRD measurements. Fig. 3b shows the evolution of the diffraction spectrum recorded in the loading direction (refer to Supplementary Fig. 3, $\Phi = 90^\circ$). The pristine TiNi was in a B19’ martensitic state, as evidenced by the B19’-TiNi (020), (111), (001), and (111) diffraction peaks. Labels “A”–“D” on the side in Fig. 3b correspond to the labels marked on the lattice strain curve of TiNi shown in Fig. 3a. Upon loading, the diffraction intensity of the (111) peak increased as the diffraction intensities of the (020), (111), and (001) peaks decreased, indicating martensite variant reorientation by detwinning. Additional evidence of the TiNi martensite variant reorientation by detwinning is shown in Fig. 3c and Supplementary Fig. 5. The detwinning deformation process of TiNi is proceeded by a relatively uniform lattice shear distortion of the martensite.

The elastic strain (lattice strain) of Ti$_3$Sn (Fig. 3a) in the loading direction rapidly increased during the stages corresponding to the initial elastic deformation and the detwinning of the TiNi, and then continued to increase at a slower rate up to 2% (Fig. 3a), which is more than six times the elastic strain of free-standing Ti$_3$Sn (approximately 0.3%) [17]. This value is also significantly superior to the elastic strains of other reinforcements (such as nanowires, laminates, and particles) embedded in conventional metal matrices, which are deformed by dislocation slip [blue circle, olive circle, dark cyan downtriangle, magenta lefttri, dark yellow righttri, navy diamond, wine pentagon, pink circle].

The strain of Ti$_3$Sn in the composite is estimated to be 4,100 MPa. This suggests that the Ti$_3$Sn is the main load bearer and significantly contributes to the strength of the composite. Such high elastic strain and outstanding load-bearing capability of Ti$_3$Sn in the composite may be attributed to the uniform martensite lattice distortion mechanism of the TiNi component and its “J-curve” deformation behavior.

It has been demonstrated recently that nanomaterials can exhibit ultra-large elastic strains when embedded in martensitic phase transforming matrix owing to the principle of lattice strain matching, in
brittle Ti$_3$Sn intermetallic compound into an in situ lamellar composite. This mechanism effectively prevents unstable ''run-away'' deformation and premature local failure, thus enabling the composite to achieve optimum ultimate strength.

The mechanical properties of our TiNi-Ti$_3$Sn composite are shown in Fig. 4, Supplementary Fig. 6. The composite exhibits a maximum ultimate compressive strength of 3 GPa and a large fracture strain that exceeds 30%, which are superior to the ultimate compressive strengths and fracture strains of other high-performance metal-based lamellar composites in which the soft component is a conventional metal (without the ''J-curve'' deformation attributes) rather than the biopolymer-like metal (''J-curve'' deformation attributes) (Fig. 4b)\textsuperscript{31–37}. In addition, the composite also exhibits a high damping capacity of the composite was characterized using a FEI-200F scanning electron microscope (SEM) operated at 20 kV.

The compression properties of the composite were tested using a servo-hydraulic materials testing system (MTS 810) at room temperature at a strain rate of 5 $\times$ 10^{-4} s^{-1}. Cylindrical compression samples with a diameter of 5 mm and a length of 10 mm were prepared according to American Society for Testing and Materials (ASTM) standards.

The damping capacity of the composite was measured using a dynamic mechanical analyzer (DMA Q800, TA) in single cantilever mode. The Love of the damping specimens was 1 $\times$ 4 $\times$ 40 mm$^3$. Damping tests were conducted at a frequency of 1 Hz in the temperature range of -130°C to 300°C with a constant heating/cooling rate of 5°C/min. Ultrasonic attenuation was measured in pulse-echo mode of a longitudinal wave using 2 MHz transducers. The ultrasonic attenuation samples were 30 mm in diameter and 30 mm in long.

In situ synchrotron high-energy X-ray diffraction (HEXRD) measurements were performed during the compression test on beamline 11-ID-C at the Advanced Photon Source, Argonne National Laboratory, USA. High-energy X-rays with an energy of 115 keV, a beam size of 0.6 $\times$ 0.6 mm$^2$ and a wavelength of 0.10798 Å were used to obtain two-dimensional (2D) diffraction patterns in the transmission configuration. Gaussian fits were employed to determine the positions of the diffraction peaks. The lattice strain for the reflection peak is calculated using $\Delta d_{hkl} / d_{hkl} = 0$, where $d_{hkl}$ is the "unstressed" lattice parameter (i.e., the peak position at zero applied stress). The error of the lattice strain measurements was less than 0.05%.

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