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Response to Comment on "Cryoforged nanotwinned titanium with ultrahigh strength and ductility"

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We address the three main points of Guo *et al.* They claim that we should have used the engineering stress versus engineering strain curves to infer the mechanical properties of our nanotwinned titanium, question our sample design on the basis of a finite-element analysis, and doubt the immobility of some preexisting grain/twin boundaries in our electron backscatter diffraction micrographs. We find their analysis to be groundless and to contain many inconsistencies.

To address Guo *et al.*'s first point (*1*) concerning Zhao *et al.* (*2*), it is important to state that in evaluating the mechanical behavior of any material, the engineering stress versus strain curve is indeed convenient, but it is not the most insightful method to demonstrate the mechanical performance of a material. When it comes to the physical understanding of the plastic deformation mechanisms and their relationship to the microstructure of a material, which was the focus of our paper, engineering stress versus strain curves are really only accurate in the elastic regime and, as such, are less useful than true stress versus true strain in characterizing the constitutive behavior in the plastic regime, where we were able to include additional data (and therefore insight) in the form of direct strain measurements. Therefore, we used true stress versus true strain curves in order to accurately characterize the strain hardening ability of the material. As the ultimate tensile strength calculated as an engineering stress is actually a "fictitious stress," the tensile strengths referred to in our paper are given as a true stress.

In our paper, we are comparing the nanotwinned Ti with its coarse-grained counterpart using the same exact sample geometry. The size of the samples that we used was primarily set by the total amount of high-quality model alloys that we had and the loading capacity of the mechanical testing instrument with the custom liquid-nitrogen LN2 stage. This limited us from making large-scale nanotwinned Ti samples that could match the ASTM standard tensile specimens. Nonetheless, we developed a small-scale sample design that was indeed robust and could be validated at room temperature (RT) via digital image correlation (DIC), as we show in detail in Fig. 1. Note that it was not our primary intention to compare our results with those from a larger-scale specimen.

From this sequence of the DIC strain maps of the RT deformed nanotwinned Ti, we can see that the von Mises strain is fairly uniform along the gauge section (orange boxed regions). No clear evidence of necking or nonuniformity exists until 50% of true strain. (Frankly, even at this late stage of deformation, the fact that the strain distribution is still rather uniform is quite impressive as compared to traditional mechanical tests of even ASTM standard size metals.) Note that the small white arrows in the map indicate the direction of the principal strain and they almost always align with the loading axis, which suggests that there is no change of the stress state. Therefore, our DIC results show that the distribution of plastic strain is constrained within the gauge section of the sample (at both the early and late stages of the deformation). This validates that our current sample design is a reasonable one. Thus, we believe that the conversion from engineering stress/strain to true stress/strain—that is, $\varepsilon_{true} = \ln(1 + \varepsilon_{engineering})$; $\sigma_{true} = \sigma_{engineering}(1 + \varepsilon_{engineering})$—is still valid. As such, the fundamental assumption for this conversion, the conservation of the volume, is valid and enables us to use true stress versus true strain as a more accurate method to describe the mechanical behavior than engineering stress versus engineering strain.

To further evaluate the effect of sample geometry on the strain distribution and the macroscopic stress-strain curves, we also conducted proof-of-concept experiments by using coarse-grained Ti and thus increasing the gauge length of the sample. The samples with different gauge lengths exhibited similar stress-strain responses. The new sample had a gauge length that was 5 times the square

root of its cross-sectional area. The results are summarized in Fig. 2.

Figure 2A displays a sample of the "standard" geometry with a gauge length 5 times the square root of the cross-sectional area, whereas Fig. 2B shows our original sample design. Figure 2, C and D, shows the DIC-measured true stress versus strain curves of the two samples and their corresponding strain hardening rates. They are almost identical, which indicates that our original sample design is reasonable. Figure 2, E and F, shows the strain maps of the two samples as a function of increasing plastic strain. Although it is true that the sample with longer gauge length indeed exhibits a smaller strain to failure than the sample that we originally used in the paper, the difference is small (~12%).

Considering the points enumerated above, we are confident that our sample design and strain calibration are reasonable at RT. For the tests conducted at 77 K, we indeed derived the strain from the recorded cross-head displacement, but the stiffness correction was not a simple elasticity subtraction; it was based on our DIC conducted at RT and calibrated over the entire loading history. This was done by constructing a one-to-one correlation (a polynomial fitting function) between the strain derived from the machine-recorded displacement and the strain measured from the DIC. Therefore, the entire displacement path is calibrated, in both the elastic region and plastic region. For the cryogenic deformation, it was not possible to perform the DIC test in the LN2 bath and so instead we made reasonable assumptions to calibrate the strain. The primary assumption was that the stiffnesses of the sample and the fixture/machine remain relatively constant at the reduced temperature. Or perhaps better put, the difference in the stiffness/compliance between the sample and other loading components remains relatively constant at cryogenic temperature. Therefore, the one-to-one fitting function can be applied to the reduced temperature. This assumption is sound for three reasons: (i) The elastic modulus of pure Ti (E_{Ti} ~ 100 GPa) is much lower than that of the tensile fixture (316 stainless steel, E_{ss} ~ 200 GPa); therefore, the major source of the measurement compliance should be from sample-machine contact, especially with the consideration that the sample fixture is ~5 times thicker than the tensile sample. (ii) The influence of the temperature on the elastic modulus is moderate between 77 K and RT. For Ti, E_{Ti} = 116 GPa at 77 K and 106 GPa at RT; for steel, the difference is almost the same. (iii) The compliance is most critical in calibrating the elastic region, whereas by comparison the compliance is negligible in the plastic region. This calibration method can be further validated by the fact that the derived modulus from the calibrated data is almost identical to theoretical values.

Guo *et al.* also argue that "the complete absence of twinning at RT that showed so strong an effect at 77 K is hard to understand." Note that although the engineering stress of the nanotwinned Ti drops slowly after yielding, this does not mean that there is "complete absence of twinning at RT." On the contrary, we did not express anything like that in our paper and therefore Guo *et al.*'s claim is not an appropriate assumption to derive from our paper. The softening effect only means that the strain hardening rate of the nanotwinned Ti saturates early at RT and some softening (recovery) mechanisms may be presented. Detwinning, or the shrinking of twin caused by the reverse motion of twin dislocations, is indeed one of the possible reasons, as it provides for plasticity but contributes little to strain hardening. However, twinning and detwinning are not necessarily exclusive; instead, they can occur simultaneously at both RT and 77 K. At 77 K, twinning quickly exceeds detwinning, which leads to a rapid increase of twin boundaries and a substantial hardening effect. At RT, however, the contribution of detwinning might be more significant as the ability to twin decreases (decreased but not absent) when temperature rises. There are, of course, other sources of softening, such as reduction of dislocation density by dynamic recovery, but details of the softening mechanisms were not the focus of our paper. Regarding Guo *et al.*'s comment on the inconsistency between detwinning and thermal stability at 673 K, this is also completely misleading, as the former is caused by reversed shear stress exerted on the twinning planes, whereas the latter simply refers to the migration rate of grain boundaries (twin boundaries in this case) subjected to a thermal field. Accordingly, they are intrinsically different mechanisms.

Guo *et al.* further conducted some finite element analysis (FEA) to "reproduce" our experiments at 77 K. Although the dimension of the model specimen was the same and they adopt the parameters from our experiments, it is not possible to use such a simple simulation to infer the complicated plastic deformation of a heterogeneous sample such as the nanotwinned Ti as described in our experiments. First, an accurate continuum constitutive relationship for the nanotwinned Ti is lacking, and there is no way that the model they used can accurately predict the plastic deformation of the material even though they claim to have extracted "constitutive parameters" from our result. Therefore, we do not believe that it is accurate to suggest that their FEA results "reproduce" our experiments. Second, although the authors failed to mention this detail, we can only assume that their FEA simulations do not take plastic anisotropy into consideration. Hence, using the same constitutive relation for each element in their FEA model cannot capture the complicated polycrystalline plasticity of a heterogeneous and anisotropic material such as the one that we studied experimentally, let

alone in a material that undergoes a complicated microstructure evolution. Moreover, even from their own FEA simulations [figure 2E of (*1*)], the nonuniform distribution and deviation of the stress state from the uniaxial stress state (stress triaxiality 0.4 to 0.5 versus 0.33) are not as "significant" as they claim (in fact, it actually decays as the plasticity proceeds and the stress triaxiality approaches 0.33 at an engineering strain of 40%). As a consequence of the complicated series of deformation mechanisms described in our paper, it is not possible for a simple constitutive relation to capture this behavior. Especially toward the later stage of the plastic deformation, their FEA model will only become less credible. For example, we show in the supplementary material of our manuscript (and Fig. 3 here again for your reference) that the 77 K–fractured sample exhibited very complex microstructure and texture within the gauge section. It is simply not possible for their simple FEA model using a single constitutive relation to capture the plastic deformation of such a complex and evolving microstructure.

It is therefore confusing to "reexamine" the deformation using their "whole specimen" length as the gauge length to calculate engineering strain. Their conclusion that there is a "50% overestimation of the deformation" is therefore unrealistic and itself an overestimate.

Finally, we will address the last point of Guo *et al.*'s comment. We found it confusing that they speculate that the microscopic strain is "nearly zero" based on a rather unscientific trace of a single grain from the electron backscattered diffraction (EBSD) scans in figure 3 of our paper (*2*). Of course, this image is only a two-dimensional projection of an evolving microstructure on the sample surface. The three-dimensional grain boundary landscape cannot be visualized, which renders their inferred "microscopic strain" from this analysis totally unfounded. Even from these traces, it is not reasonable to conclude that the microscopic strain is zero and that the "only change was the density of twins with increase in strain," as the shape and curvature of the grain boundaries indeed have changed, especially toward the later stage of the plastic deformation. In fact, Guo *et al.* themselves acknowledge that the density of the twins has changed drastically. It is a contradiction to state that there is zero microscopic strain with so much twinning occurring at the same time, because a twin by definition provides shape change to a crystal lattice. Moreover, as plastic deformation proceeds, the grains reorient because of the continuous twinning, and the "grain" is actually crystallographically different from its initial structure, rendering Guo *et al.*'s technique for inferring microscopic strain meaningless. As an analogy, this is equivalent to saying that the length of a caterpillar and butterfly are the same, hence nothing has changed. But of course, the structure of the insect has changed inside, rendering the measurement of the length insufficient to describe any actual change. Therefore, it is entirely inappropriate for Guo *et al.* to state that our observation is "troubling." Note that the primary goal of this sequence of EBSD analysis was to demonstrate that nanotwinned titanium has a variety of twinning systems including, but not limited to, the ones that we show in our paper to accommodate plastic strain at reduced temperatures. Although they are representative, it does not mean that all other grains will behave in the same way.

Regarding the comment on the mobility of the $\{11\bar{2}2\}$ twin, Guo *et al.* simply argue that the critical resolved shear stress (CRSS) for the twin is low enough to be activated at a high stress state at 77 K. Although this is true, it only means that new twins can be generated when the orientation is favorable but cannot be the sole reason that the existing twin will indefinitely grow or move. Similar to dislocation slip, the choice of twinning systems depends heavily on the local stress state, and certain twin variants are preferred because of a higher Schmid factor in those particular grains. The immobility of the preexisting $\{11\bar{2}2\}$ twin could be a result of less favored orientation with respect to the loading (the same rationale also applies for the $\{10\bar{1}2\}$ twin). A recent study shows that twins with moderate Schmid factors are relatively static during the loading process (*3*). Twinning in hexagonal close-packed metals can be more complicated than this, as it is usually associated with strain accommodation in the immediate vicinity of the twins, which often triggers secondary twinning or deformation in the neighboring grains. Such complicated "non-Schmid" effects have been reported by Qin and Jonas (*4*). These subtle effects are of course important but are beyond the scope of our paper. Therefore, it is unfounded to determine the motion of twins simply by arguing the low CRSS without taking the local stress state and compatibility into consideration.

Additionally, Guo *et al.* referenced one of their own papers that used micropillar testing to measure the CRSS. However, this idealized measurement is irrelevant to our scenario; the initial microstructure, specimen size, stress state, and loading conditions are drastically different. In addition, as a result of size effects and Ga damage from focused ion beam microfabrication, their micropillar measurements that they refer to cannot be considered to be a "nearly defect-free" state, as they claim.

We thank Guo *et al.* for their interest in our work and have carefully considered the specific points in their comments. However, we find them to be groundless and to contain many inconsistencies. We hope that readers will agree with our analysis of these technical considerations.

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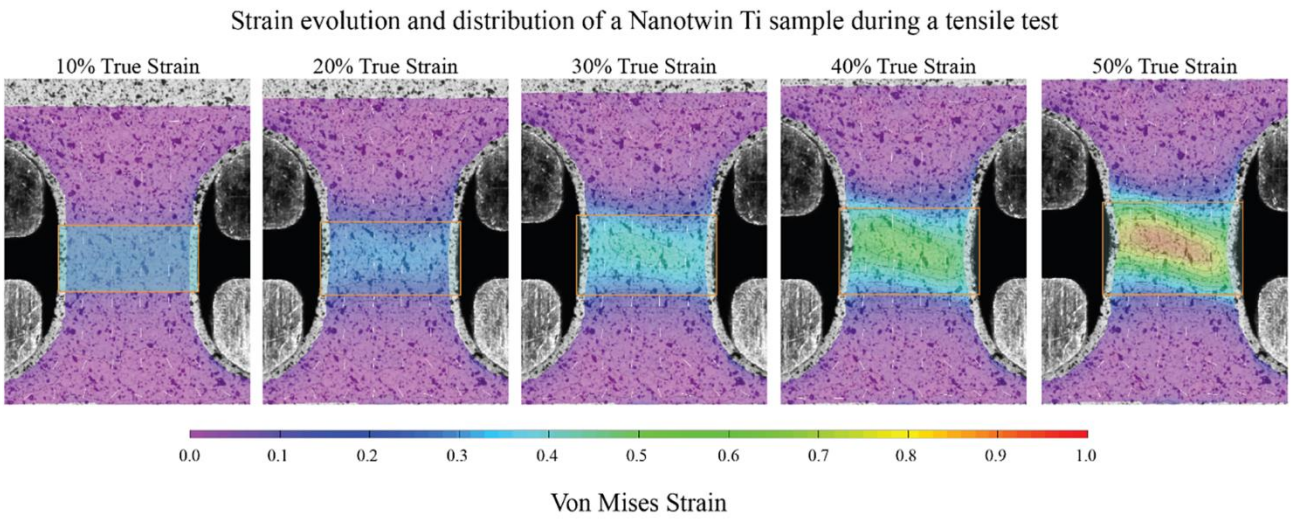

Fig. 1. Strain evolution and distribution of a nanotwinned Ti sample during tensile experiment at room temperature.

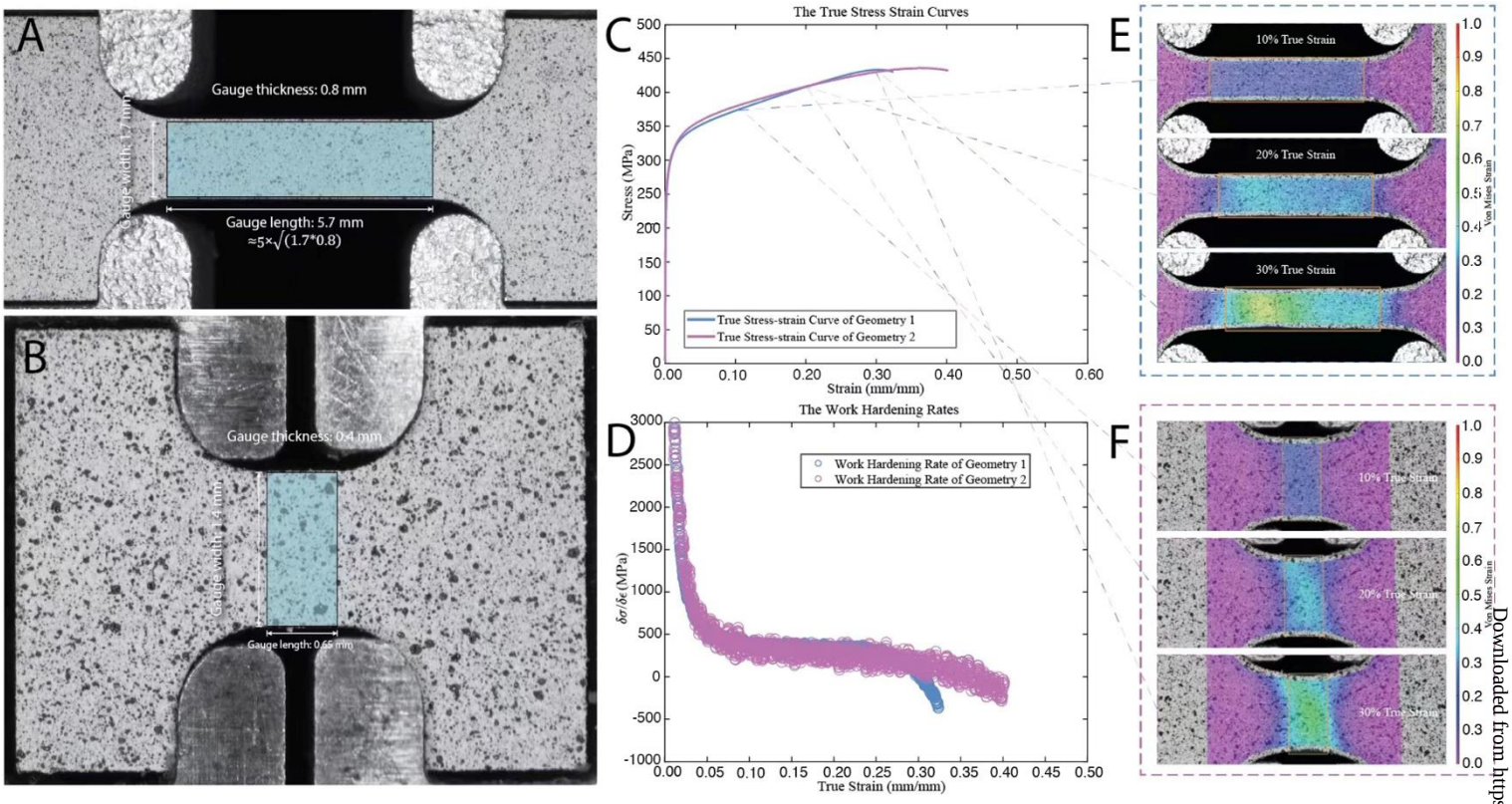

Fig. 2. Influence of the gauge dimension on the mechanical properties. (**A**) "Standard" sample with gauge length 5 times that of the square root of the cross-sectional area. (**B**) Sample used in the current investigation. (**C** and **D**) Comparison of the true stress versus strain curves and their corresponding strain–hardening rate curves. (**E** and **F**) Two-dimensional strain maps of the two samples at different strain levels. The highly overlapped stress-strain curves and strain–hardening rate curves show that the geometry of the sample in our investigation is certainly reasonable. DIC strain maps also show that necking did not occur, in both sample geometries, until the late stage of plastic deformation.

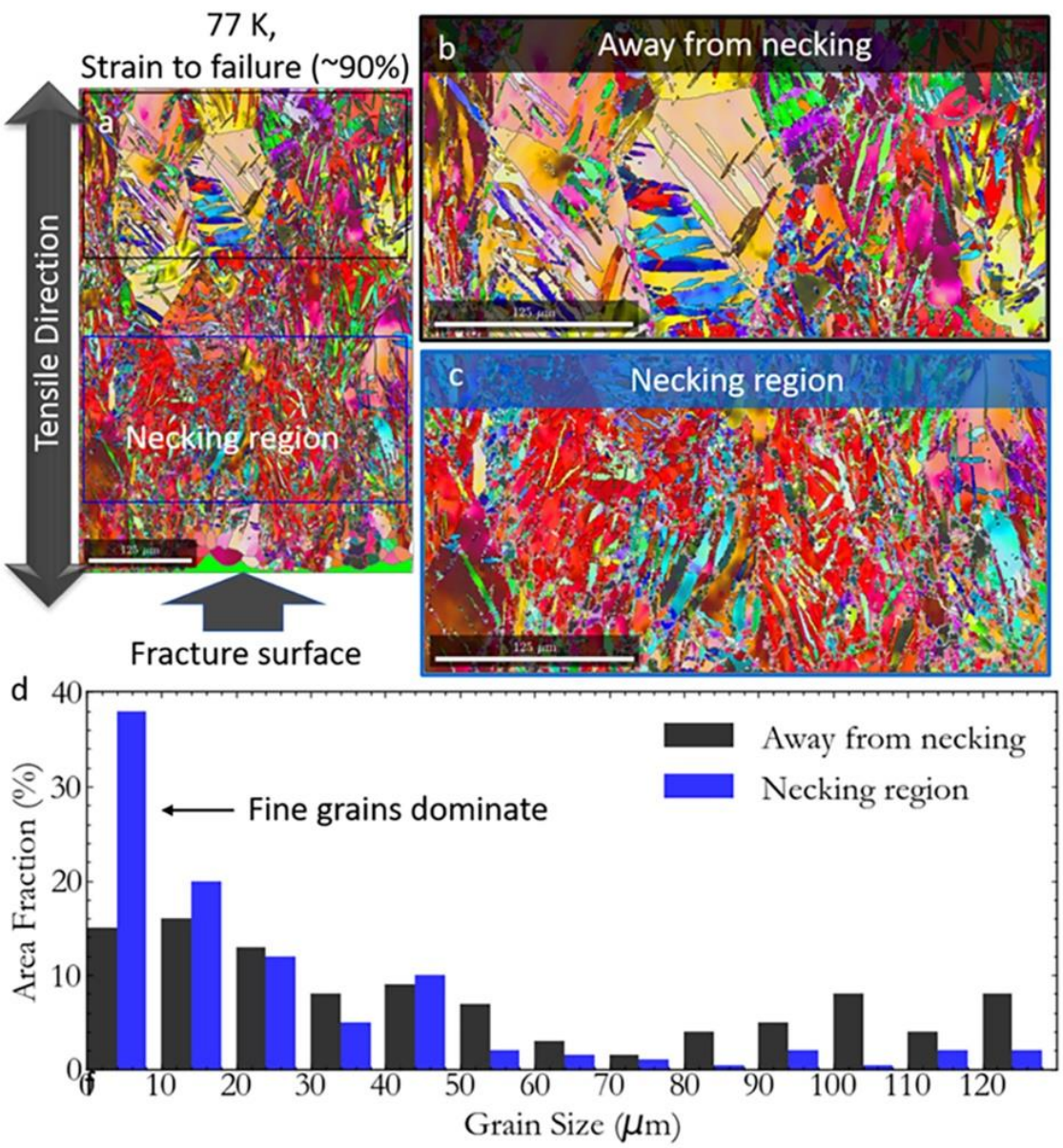

Fig. 3. EBSD/inverse pole figure mapping of the sample fractured at 77 K. (A) Overview of sample gauge section. (B and C) Higher magnifications of regions slightly away from the necking (B) and at the region of necking (C). (D) The comparison suggests that the plastic strain is severely localized in the region where the sample becomes narrower, leading to a much-refined grain size. Scale bars in (A) to (C), 125 μm.

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