On capturing the grain-scale elastic and plastic anisotropy of alpha-Ti with spherical nanoindentation and electron back-scattered diffraction

Authors:

Jordan S. Weaver^{1,2}, Matthew W. Priddy², David L. McDowell², Surya R. Kalidindi^{2*}

¹Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM, USA

²George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA

*Corresponding author. Tel.: +1 404 385 2886.

E-mail address: surya.kalidindi@me.gatech.edu (S.R. Kalidindi).

URL: <http://mined.gatech.edu/>

Abstract:

Spherical nanoindentation combined with electron back-scattered diffraction has been employed to characterize the grain-scale elastic and plastic anisotropy of single crystal alpha-Ti of two different compositions (in two different titanium alloys). Data analyses protocols needed to reliably extract the desired properties of interest are extended and demonstrated in this paper. Specifically, the grain-scale mechanical response is extracted in the form of indentation stress-strain curves for commercially pure (CP-Ti) alpha-Ti and alloyed (Ti-64) titanium from measurements on polycrystalline samples. The results are compared with responses of single crystals and nanoindentation tests (hardness and modulus) from the literature, and the measured indentation moduli are validated using crystal-elastic finite element simulations. The results obtained in this study show that (i) it is possible to characterize reliably the elastic and plastic anisotropy of alpha-Ti (hcp) of varying alloying contents with spherical nanoindentation stress-strain curves, (ii) the indentation modulus of alpha-Ti-64 is 5-10% less than CP-Ti, and (iii) the indentation yield strength of alpha-Ti-64 is 50 to 80% higher than CP-Ti.

Key Words:

Hertzian indentation, stress and strain, pop-ins, hcp metals, finite element

1. Introduction

Titanium alloys offer excellent mechanical properties (strength and fatigue life) and corrosion resistance, particularly relevant to light weighting applications [1, 2]. Titanium alloys also exhibit a rich variety of possible microstructures with varying amounts and morphologies of α (hcp) and β (bcc) phases. For example, the alloy Ti-6Al-4V (Ti-64) has microstructures that can be categorized into equiaxed (small amounts of β at α -grain boundaries), lamellar (disc like, alternating α and β grains forming colonies), and duplex (mixture of both) (e.g., [3]). The properties of α/β alloys are ultimately linked to the microstructure, and the microstructure can be tuned or designed for improved performance. However, the computational tools used for the microstructure-sensitive design of Ti alloys [4-8] necessitate estimates of the elastic and plastic anisotropy of the constituent phases. For materials like Ti exhibiting multiple slip systems with varying degrees of shear resistance, this typically comes from single crystal experiments [9-12] which require significant effort and are not possible for all chemical compositions due to the difficulty in producing large single crystal specimens. Alternatively, focused-ion beam (FIB) techniques can be used to prepare samples (micropillars [13-16] and cantilever beams [17, 18]) and mechanically test individual phases and orientations in Ti alloys. However, this also requires significant effort and specialized equipment; moreover, in some cases, these samples have substantial ion-beam damage [19].

Alternatively, nanoindentation has been used to mechanically characterize individual phases in Ti alloys with significantly less effort and equipment [20-29]. Typically, these tests result in measured modulus and hardness values for different grain orientations. However, the results in the literature for both properties are often inconsistent and do not exhibit the expected mechanical anisotropy. Many have reported no elastic anisotropy when measured using the

unloading curve for nanoindentation [20, 23-28]; the most likely reasons for this are the test and data analyses protocols used in the studies. The material under the indenter has undergone significant plastic deformation prior to unloading, and therefore properties estimated from the unloading segments are indeed affected by the plasticity induced in the indentation itself. Britton et al. [21] managed to capture some elastic anisotropy of commercially pure titanium (CP-Ti), but the range was smaller than expected compared to modulus measurements of single crystals [12]. Kwon et al. [25] also reported an orientation dependence but the absolute values are significantly higher than other modulus estimates in the literature [30].

In addition, there are conflicting reports for hardness, particularly for CP-Ti. For example, significantly different values have been reported for the same grade and similar conditions (annealed) of CP-Ti: 0.75-1.0 GPa [22] and 2.9 ± 0.4 GPa [23]. Again, this is likely due to differences in test procedures. Hardness often depends on the applied load, and in the case of nanoindentation [31], it also depends on accurately capturing the effect of the sink-in or pile-up of material around the indenter. Conflicting trends in hardness are also seen while comparing different grades of pure Ti in similar conditions (annealed) with different yield strengths (due to differences in interstitial oxygen content). Specifically, the reported hardness values, arranged highest to lowest, are grade 1 (4.4-5.5 GPa) [21], high purity (1.6-1.87 GPa) [20], and grade 2 (0.75-1.0 GPa) [22]. Whereas, the expected trend (highest to lowest hardness) based on uniaxial strength [1] would be a completely different order: grade 2, grade 1, and high purity Ti.

Indentation size effect has been reported and discussed extensively in literature [32-34]. This effect is most clearly observed at low loads and small indentation zone length scales, and is attributed largely to the high density of geometrically necessary dislocations needed to accommodate the strong plastic strain gradients involved in such experiments. At larger

indentation depths (e.g., > 50 nm), this effect is generally not observed (i.e., hardness values plateau). In the view of the authors, hardness values are most useful as comparative measures of the material's resistance to plastic deformation. It is only reasonable that hardness values obtained using different indentation shapes and depths are not consistent with each other (as an example, one could argue that hardness estimates at different indentation depths would correspond to different points on the material's stress-strain response). Recent advances in spherical nanoindentation protocols discussed next address some of these issues and provide a more reliable characterization of the mechanical response [35, 36], as discussed next.

Kalidindi and Pathak [35, 36] developed analysis protocols for spherical indentation that capture the material response in the form of an indentation stress-strain curve. A brief summary is provided in Section 3, and additional details, including some improvements, can be found in the supplemental material. It is important to note that these new test procedures measure the indentation modulus from the initial loading curve prior to plastic deformation, and the estimate of strength comes from the elastic-plastic transition on an effective indentation stress-strain curve. Hence, their method: 1) captures the response of the virgin material, and 2) captures the initial flow stress and hardening as opposed to the flow stress at finite, indiscriminate, effective strains (i.e., hardness). [It was demonstrated that the measured indentation yield strengths using these protocols are not very sensitive to changes in the indenter size \[37-40\], for the range of indenter sizes studied.](#) Note that the initial flow stress and rate of work hardening are not easily extracted directly from the load-displacement curve in traditional indentation tests because it is hidden in the early stages of loading [35]. These new protocols represent a major advance in moving to a more quantitative and rigorous analysis of nanoindentation tests. The extraction of material properties or model parameters can then be achieved through coupling of experiments

and simulations. Currently, the models for extracting material properties are limited to ideal materials (isotropic elastic-plastic with linear hardening) and anisotropic elasticity of cubic crystals [41-43]. Such models and protocols for hcp crystals are an area of current work and are critically needed.

In this study, we first measure the orientation dependent elastic and plastic mechanical response of CP-Ti with hcp crystal structure using the recently developed spherical nanoindentation protocols mentioned above. The same is then done for alloyed hcp α -Ti in Ti-64 (α -Ti-64). It will be demonstrated that these protocols can reliably and quantitatively measure the elastic and plastic anisotropy (indentation modulus and yield strength) of Ti alloys compared to traditional nanoindentation protocols (modulus and hardness). In addition, the sensitivity of the indentation stress-strain response (e.g., indentation yield strength) to alloying content will be demonstrated for the first time through a comprehensive study of α -Ti. The experimental indentation modulus results were compared with a 3-D crystal-elastic finite element indentation model using reported elastic constants in literature. The limitations of these protocols are discussed.

2. Details of Experiments and Simulations

2.1 Nanoindentation Experiments

Grade 2 CP-Ti and grade 5 Ti-6Al-4V (Ti-64) were obtained in bar form from McMaster-Carr. The expected chemical compositions of the α -phase for both materials are listed in

Tables

Table 1 [44, 45]. The stock material was annealed to remove effects of any prior cold work and grow the grain or features size slightly to avoid grain boundaries during the indentation tests. CP-Ti was annealed at 800°C for 2 hours and furnace cooled. Ti-64 was annealed at 1025°C for 2 hours, slowly cooled (0.1°C/min) to 950°C where it was held for 1 hour and then furnace cooled. The resultant microstructures of each material are shown in Figure 1. The average grain diameter determined from electron backscatter diffraction (EBSD) was 27 μm for CP-Ti and 25 μm for Ti-64 (including the α - β colony grains) determined from large scans (>2000 grains). The grain size distribution for CP-Ti included grains larger than 100 μm as evident in the micrographs in Figure 1. The average in-grain misorientation in both materials was less than a degree. The spherical nanoindentation stress-strain protocols have been shown to be highly sensitive to any residual deformation on the surface, and typically a final electropolishing step is performed to remove any remaining damaged layer from mechanical polishing [46]. In addition, the oxygen rich layer due to heat treating was removed by careful sectioning and grinding. This was followed by polishing down to a 0.06 μm colloidal silica suspension. A final step of electropolishing with a perchloric acid based electrolyte at -15 °C for 0.5 to 5 mins under constant voltage (20-25 V) was used to produce pristine surfaces for nanoindentation.

Indentation sites were carefully selected inside grains away from boundaries for select orientations identified from EBSD maps using a Tescan Mira XMH FE-SEM and EDAX Hikari EBSD camera. Indentation was performed with diamond conical-spherical tips with nominal radii of 16.5 and 100 μm on an Agilent G200 Nanoindenter using an XP head with the continuous stiffness measurement (CSM) module. The CSM performs many small unloads with a superimposed harmonic signal on the prescribed monotonic loading [47, 48]. Tests were run

with a constant strain rate (loading rate divided by the load) of 0.05 s^{-1} to maximum depths of 300 nm (CP-Ti, 16 μm radius), 400-500 nm (CP-Ti, 100 μm radius), and 450 nm (Ti-64, 16 μm radius). CSM was run at a displacement amplitude and oscillation of 2 nm and 45 Hz [49]. The CSM is critical for estimating the contact radius throughout the test. Once plastic deformation occurs, Hertz's equation can no longer be applied to the loading curve. Rather, the unloading curve, which is a primarily elastic response, is required. The contact radius is determined directly from Hertz's equations using the unloading stiffness from CSM and the measured indentation modulus (as determined from the initial loading curve). Two indenter sizes were used for CP-Ti in order to establish a reliable method for determining the indentation yield strength in the event of relatively small pop-ins. This will be detailed in Section 3. Comparisons between indentation stress-strain curves of CP-Ti and α -Ti-64 were then made for tests with the 16.5 μm radius indenter.

2.2 Crystal Elastic Finite Element Simulations

To provide estimates of the indentation modulus for various loading orientations, FEM simulations of the indentation were performed using an anisotropic elastic material model. Titanium and other hcp metals exhibit a transversely isotropic elastic response, meaning five independent (six total) elastic constants are needed to fully describe their elastic response. For the simulations, the spherical nanoindentation experiments were idealized as single crystal specimens contacted by a rigid, frictionless spherical indenter. Frictionless conditions have been determined in previous studies as a sufficient assumption for blunt indenter tips such as spheres [42, 50-52]. These simulations were performed using ABAQUS/standard 6.10-1 [53].

The mesh configuration used in this work, Figure 2, is three-dimensional and consists of a combination of hexahedral and tetrahedral elements. The hexahedral elements, located directly

beneath the indenter, have a width of 10 nm and a height of 20 nm. Tetrahedral elements are employed outside of the region of contact and high stress to improve computational efficiency. The overall dimensions of the single crystal specimen are 3.0 x 3.0 x 4.0 microns (width, depth, and height), and the size of the hexahedral region is 0.40 x 0.40 x 0.80 microns. The hexahedral region contains 64,000 C3D8 elements while the tetrahedral region contains 92,838 C3D4 elements [53]. The radius of the indenter is 13.5 microns. The indenter was displaced in the z-direction, the negative z-face of the single crystal specimen was held motionless in all directions, and the x- and y-faces are traction-free. To estimate the indentation modulus, a single load-unload of the indenter was performed to 1 nm and 0.25 nm, respectively. The unloading data followed the loading data as expected for fully elastic loading. The full simulation was used to determine the indentation modulus, E_{ind} , from the load and displacement data according to Hertz's Theory [35, 54].

3. Indentation Data Analyses

The measured load, displacement, and stiffness data were converted to indentation stress-strain curves following the protocols of Kalidindi and Pathak [35]. Some important details of the analyses protocols are summarized in the supplemental material. Examples of the load-displacement and indentation stress-strain curves for CP-Ti obtained using two different indenter tip radii are shown in Figure 3. The indentation modulus is determined from the initial elastic load and displacement data after the zero point correction [35]. Although the analysis (based on Hertz's Theory [54]) was originally intended for an elastically isotropic material, it has been shown that the same approach can be extended to elastically anisotropic materials with the understanding that the modulus extracted represents an “effective” value in the indentation direction [42, 55-60]. In other words, the equation for indentation modulus can be expressed as

$$\frac{1}{E_{eff}} = \frac{1}{E_{ind}} + \frac{1 - \nu_i^2}{E_i} \quad (1)$$

where E_{ind} denotes the indentation modulus in the crystallographic direction parallel to the indentation direction. E_{ind} is expected to be a function of the crystal orientation. An indenter modulus, E_i , and Poisson's ratio, ν_i , of 1140 GPa and 0.07 were used in accordance with the properties of diamond [31, 57] .

The indentation yield strength is defined using a 0.2% strain offset on the indentation stress-strain curve. Pop-ins or displacement/strain bursts relate to the difficulty of activating dislocation sources [61-63]. These occur commonly in annealed metals with indenter radii on the order of 10 μm and below [39, 40, 46, 61-63]. The pop-in masks the indentation yield point. For Fe-3%Si and Al it has been demonstrated that the indentation yield strength can be estimated by a back extrapolation of the indentation stress-strain data in the plastic regime [37-40]. The main observation that supports this procedure is that the indentation stress-strain curves for a single grain with and without a pop-in are nearly identical, with the same indentation yield strength. This holds for tests with the same indenter size as well as tests with significantly different indenter sizes (e.g., 10 and 100 μm radii). The back extrapolation approach was used to determine the indentation yield strength for tests with pop-in, as illustrated in Figure 3. The initial hardening slope was similarly determined based on a linear regression of the indentation stress-strain data in the plastic regime. Specifically, it was determined between the 0.2% indentation yield strength and a strain offset of 2-2.5%. In the event of a pop-in, the regression started at the data immediately following the pop-in. In this scenario, the back extrapolation and hardening slope regressions are exactly the same. Consequently, tests with particularly large pop-ins (greater than 2% strain) were not used to estimate plastic properties. The ratio of the

measured indentation stresses before and after the pop-in was computed and reported in this paper as an indicator of the size of the pop-in event.

In this study, we have also tried to incorporate some estimates of the variance or uncertainty in the estimated indentation properties. We pay specific attention to two sources of variance and uncertainty in the measurements reported here. The first source reflects the location to location variability in the material structure in the indentation zone (e.g., reflecting the differences in dislocation structures in different regions within the same grain). This is addressed, where feasible, by placing multiple indents inside the same feature (i.e., grain), and the uncertainty in the measured property is recorded through the variations between measurements. Given the relatively small grain size in our samples, only a few indents (sometimes just one) could be placed inside selected grains. The second source of uncertainty comes from the selection of parameters (or other choices) in the analyses of the single test. More specifically, the indentation stress-strain protocols employed involve a selection of the initial elastic segment, which then controls the zero-point correction. Variations in the selection of this initial elastic segment result in small variations in the indentation stress-strain curve and the extracted indentation properties. The standard deviations (and the error bars) reported in this work include both sources of variance described above. In other words, when multiple tests were performed in the same grain, a pooled variance of the analyses is determined and reported in this work.

4. Results

4.1 Commercially Pure Ti

The indentation modulus versus the crystal c-axis declination angle, Φ (the middle angle in the set of Bunge-Euler angles $(\varphi_1, \Phi, \varphi_2)$) used to describe the crystal lattice orientation with

respect to the sample reference frame [64]) is shown in Figure 4 for two indenter sizes (16 and 100 μm radius). As for the single crystal elastic modulus, the stiffest orientation is observed to be along the c-axis ($\Phi = 0^\circ$), while the fully declined orientation corresponded to the most compliant direction ($\Phi = 90^\circ$). Because of transverse isotropy of elastic stiffness in the crystal reference frame (captured by the φ_2 rotation) and the fact that any rotation of the sample around the indentation direction (captured by the φ_1 rotation) will not influence the indentation modulus, we can infer that the indentation modulus should depend only on Φ (i.e., no dependence is expected on (φ_1, φ_2)). Indeed, crystal elastic finite element simulations show no dependence on either angle. It is also observed that measurements with 16 and 100 μm tip radii (colored as blue and red, respectively, in Figure 4) are highly consistent with each other.

Crystal elasticity finite element simulations of spherical indentation were performed using a set of single crystal elastic constants taken from literature [12] to determine the indentation modulus (C_{11} , C_{12} , C_{13} , C_{33} , and $C_{44} = 162.2$, 91.8 , 68.8 , 180.5 , and 46.7 GPa respectively). The simulations and experiments are in fairly good agreement with the most deviation occurring for fully inclined and declined orientations. This would suggest that a slightly modified set of elastic constants should be used; such tuning of the elastic constants to fit the experimental data better has not been explored in this study.

Extending the reasoning above, we can infer that the indentation yield strength should depend only on (Φ, φ_2) (i.e., no dependence on φ_1) [37, 42]. Unlike indentation modulus, some dependence on φ_2 is expected because the resolved shear stress on different slip systems will change with φ_2 . Figure 5 depicts the orientation dependence of indentation yield strength in multiple plots. It can be seen from these plots that indentation yield strength in the materials tested here also depends primarily on the declination angle. Furthermore, indents along the c-axis

exhibit the highest strength as expected (c-axis orientations are expected to be the hardest orientations [20-28]).

The available modes of inelastic deformation in CP-Ti include prismatic, basal, and pyramidal slip, as well as extension and contraction twinning [3, 6, 21, 22, 65-70]. It is relatively easy to see that the pyramidal $\vec{c} + \vec{a}$ slip system is the most favorable slip system for indentation along the c-axis [25, 71]. However, this is also the most difficult slip system (about 2.5-15 times more difficult to activate compared to the prismatic slip system [72, 73]). As the declination angle increases to over 40 degrees, it is clear that prismatic slip is favorably oriented and the most likely activated slip system (e.g., [65, 67]). Indeed, the stress field under the indenter is highly heterogeneous, and the activation of multiple slip systems has been reported for all orientations [25, 26]. Even so, the simple explanation presented above suffices to explain why there is a maximum in indentation strength for the c-axis crystals, which then gradually decreases with an increase in the declination angle.

Results shown in Figure 5 for the two different indenter sizes agree well with each other (the differences are within the uncertainty in the measurements). One might infer that the measurements with the 16 μm radius tip show marginally higher values and more variance compared to the measurements from the 100 μm radius indents. This is partly due to the larger pop-ins observed in the tests with the 16 μm radius indenter (these require back extrapolation for the estimation of the indentation yield strength) and partly because the variance should indeed be expected to be higher in the measurements at the lower length scales (the material internal structure in the smaller indentation zones is expected to exhibit more variance naturally).

Recent work by Pathak et al. [74] on zirconium, using similar protocols as those described here, has shown a size effect on the indentation stress-strain response that might be

attributed to a size effect of deformation twinning. Characteristics associated with deformation twinning (e.g., high hardening rates, appearance of twin-like structures on the surface at or near the indentation sites) were observed in that study only for the indents with the larger tips (e.g., 100 μm radius indenter and above). CP-Ti readily twins in bulk uniaxial tests [68, 75, 76]. Interestingly enough, the indentation stress-strain response and the post-test micrographs of indentation sites from the present study (see Figure 6) do not show the same behavior observed in tests using a 100 μm radius indenter on Zr. This would appear to indicate a lack of twinning for the experiments in Ti reported here. There are significant differences between Ti and Zr in terms of slip resistance between different slip systems. The ratio of $\vec{c} + \vec{a}$ slip to prismatic slip resistances is reported to be ~ 3 for Ti [4] and ~ 10 for Zr [77]. Basal slip resistance is only slightly higher than the prismatic slip resistance in Ti [66], while it is difficult to non-existent in Zr [77, 78]. In both metals, deformation twinning and $\vec{c} + \vec{a}$ slip are known to be the hardest modes of plastic deformation [72, 77]. Furthermore, deformation twinning is known to exhibit significant size dependence [13, 76, 79, 80], which is highly consistent with the observations in the indentation tests discussed above on Zr samples. Based on this rationale, it is possible that indentation tests on Ti samples may exhibit deformation twinning at larger indenter sizes; since twinning also depends on tensile versus compressive stress state, this also affects prospects for twinning under indentation.

Figure 6 does show slip lines that appear outside the residual indent which indicate primarily prismatic slip in these regions and a change in shape of the residual indent with crystal orientation. These observations and the lack of twinning evidence in CP-Ti are consistent with observations in literature [22, 25]. In the case of indentation along the c-axis, the residual indent is nearly equiaxed, which is attributed largely to the hexagonal crystal symmetry about the

indentation axis. However, when indenting at significant declination with respect to the c-axis, the residual indent is discernably nonequiaxed. Furthermore, the short axis of the residual indent is typically coplanar with the c-axis (see the residual indents and the c-axis orientations in Figure 6). This is consistent with the expectation that c-axis presents a hard direction for plasticity (for both contraction and extension). This deviation from a circular contact may introduce some error in the estimation of the contact area using Hertz's equations. However, the error is likely small because the linear relationship between h and $P^{\frac{2}{3}}$ (expected in Hertz's theory) appears to hold true even for various classes of elastically anisotropic materials (resulting in non-circular contact area) [42, 55, 56, 60]. Indeed, some researchers have evaluated the error associated with circular/non-circular contact, and they concluded it has a negligible effect on the elastic properties (e.g., [58]). Since the experiments in this work are carried out to only moderate plastic strains, the error is also likely negligible. However, one should pay particular attention to this factor for indents to very large depths and substantial corresponding plastic strain levels.

4.2 Alloyed Ti

Figure 7 presents the measured indentation modulus results with a 16 μm radius tip on alloyed Ti (α -Ti-64). The measurements are compared to finite element simulation results obtained using available single crystal elastic constants from literature [30] for similarly alloyed α -Ti (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} = 136, 163, 78.0, 68.5, 40.6 GPa for Ti-6wt.% Al and = 141, 163, 76.9, 57.9, 48.7 GPa for α -Ti in Ti 6wt.%Al-2wt.%Sn-4wt.%Zr-2wt.%Mo). The experiments and simulations are in reasonable agreement, and suggest that it should be possible to fine tune the single crystal elastic constants to improve the agreement between the experiments and the models. The orientation dependence in α -Ti-64 is indeed very similar to the trend seen previously in CP-Ti. However, the indentation modulus of α -Ti-64 is reduced by approximately

5% along the c-axis and 10% for fully declined orientations, compared to CP-Ti. The measured elastic constants from Kim and Rokhlin [30] as well as first principle calculations [81, 82] support the statement that α -Ti-64 is more compliant than CP α -Ti. This is despite the fact that the Young's modulus for polycrystalline Ti-64 (114 GPa) is generally reported to be about 8% higher than CP-Ti (105 GPa) [83]. The precise role of β -Ti in both the elastic and plastic properties of Ti-64 is not yet fully understood.

Figure 8 summarizes the measured orientation dependence of the indentation yield strength and compares the indentation stress-strain responses of α -Ti-64 with CP-Ti for similarly oriented crystals. The orientation dependence of indentation yield strength observed in α -Ti-64 exhibits the same trend seen earlier for CP-Ti (shown in Figure 5). However, the indentation strength has increased by a factor of about 1.5 for the c-axis oriented crystals and 1.8 for fully declined crystals. The oxygen content between the two materials is similar, so that the increase in strength is primarily due to the addition of Al. Al is known to increase the slip resistance of prismatic, basal, and pyramidal slip systems with the greatest effect on prismatic slip [9]. This supports the observed overall increase in strength as well as the higher percentage increase in strength for crystals favorably oriented for prismatic slip ($\Phi = 90^\circ$). The simulations and experiments on polycrystalline CP-Ti and Ti-64 samples by Fundenberger et al. [72] arrived at the same ratio of basal to prism slip resistance and a 10% reduction in the ratio of pyramidal to prism slip resistance for Ti-64 compared to CP-Ti. The present observations are in accordance with these previous studies. Most importantly, the results presented here indicate that the indentation stress-strain curves and indentation yield strength are indeed highly sensitive to the changes in alloying content, and the observed trends are in good agreement with single and polycrystalline studies of CP-Ti and Ti-64.

The measured orientation dependence of the indentation initial hardening rates, the pop-in stresses, and ratio of after pop-in stress to the pop-in stress in both α -Ti-64 and CP-Ti are summarized in Figure 9. The indentation initial hardening rates for α -Ti-64 are significantly higher compared to CP-Ti, although there is considerably more scatter in these measurements compared to the scatter in the measurements of indentation modulus or indentation strength. The protocols for the extraction of hardening rates from indentation stress-strain curves are still being developed; the comparison presented here should be considered to be only qualitative at this time.

Figure 9 also indicates that the pop-in stresses measured in α -Ti-64 are significantly higher than those measured in CP-Ti. Note also that there is considerable scatter in the measured pop-in stress, indicating the observed pop-ins are indeed highly stochastic in the indentation experiments. In both materials, the pop-in stresses for c-axis oriented crystals are the highest, and the pop-in stresses decreased with increase of the declination angle. Since the difficulty of establishing persistent dislocation sources is the main factor controlling pop-ins, these observations are consistent with the earlier discussion on the increased slip resistances in the alloyed α -Ti-64 compared to CP-Ti and the need to activate the much more difficult pyramidal $\vec{c} + \vec{a}$ slip system. Interestingly, the ratio of the stress before and after a pop-in is somewhat higher in CP-Ti compared to α -Ti-64.

We believe that the observations of increased indentation hardening rates in α -Ti-64 and the larger pop-ins in CP-Ti are both indirect consequences of the length scale effects in indentation measurements. Our analysis has indicated that the volume of material probed in CP-Ti indents in the experiments reported here is significantly smaller than in the corresponding indents on α -Ti-64. More specifically, the average contact radius at yield is estimated to be about

500 nm for the indents in CP-Ti versus about 800 nm for the indents in α -Ti-64; this is a direct consequence of the observation that the indentation modulus is about the same in the two materials, but the indentation strength in the alloyed Ti is significantly higher. Smaller indentation length scales have indeed been previously reported to promote larger pop-ins and lower initial hardening rates [38, 46, 61].

5. Discussion

This discussion is mainly focused on the relative merits of employing the spherical nanoindentation stress-strain protocols to estimate anisotropic elastic and plastic properties of α -Ti. A summary of the prior literature on properties (modulus and hardness) measured from nanoindentation of α -Ti for pure and alloyed (Ti-64) Ti is provided in

Table 2. The results (indentation modulus and yield strength) from this study are also added for comparison. In order to compare modulus measurements directly, the reported values of sample or Young's modulus from the Oliver-Pharr method [31] have been converted back to indentation modulus using an Poisson's ratio of 0.3 and Equation (1). In the table, the values of modulus and hardness are presented for orientations with the c-axis nearly parallel with the indentation axis ($\Phi=0^\circ$) and near selected declinations ($\Phi=45^\circ$ and 90°) for each study. For fully declined orientations ($\Phi=90^\circ$), indents with the surface normal near $[\bar{1}\bar{1}20]$ and $[0\bar{1}10]$ have been separated, although most studies show no difference.

5.1 Elastic Anisotropy

Table 2 indicates that most of the previously reported values do not capture the orientation dependence of indentation modulus in any meaningful or systematic manner. Based on the crystal elastic finite element simulations in this work, it is also apparent that the differences in the magnitudes of the indentation modulus are indeed significant (e.g., 198 to 137 GPa for alloyed α -Ti). The main reason for not capturing this important orientation dependence in prior studies is, in our opinion, directly related to the protocols used in these studies. First, the Berkovich tip produces a large amount of plastic deformation. The indentation modulus extracted from the unloading segment (after inducing a large amount of plastic deformation in the loading segment) is then a measure of a heavily deformed (no longer virgin material) volume. The plastic deformation is likely high enough to cause grain distortion and rotation at the indentation site as evidenced in the distortion and re-orientation of piled-up material [21, 22]. Second, it has been observed that the pile-up and sink-in behavior of material at the indentation site is material and orientation dependent [21, 22, 31]. Corrections must then be made to the area function in order to accurately measure modulus and hardness. It is not clear how significant these errors are, but they likely contribute to the confusion over reported values for indentation modulus. In stark contrast, the spherical nanoindentation protocols used in this work are not subject to these errors. The determination of the indentation modulus comes from the initial elastic loading segment prior to plastic deformation at the indentation site. In addition, no area function is used. The contact area (radius) is determined directly from the continuous stiffness measurement using the measured indentation modulus. The modulus is assumed to be constant throughout the test. This is a reasonable assumption given that the amount of plastic deformation is relatively small compared to Berkovich indentation.

5.2 Plastic Anisotropy

Most authors report a significant orientation dependence of hardness, as summarized in

Table 2. Hardness is a qualitative measure of flow stress partly because it corresponds to an indeterminate, somewhat arbitrary effective strain. In order to address this issue of an arbitrary strain, test parameters are often standardized (e.g., maximum load), the average value over a range of indentation depth is reported, or hardness versus depth curves are reported. We reason that the effective plastic deformation associated with the hardness measurements in

Table 2 is significantly higher than those pertaining to the spherical indentation stress-strain curves in this study. Therefore the traditional hardness values estimate the flow stress after significant plastic deformation has occurred. Again, in stark contrast, the indentation yield strength determined using the indentation stress-strain curves is an estimate of the initial flow stress or strength. It also has the advantage of being independent of test parameters (e.g., maximum load). Indentation yield strength is thus more physically relevant than hardness for calibrating plastic model parameters such as slip resistances. The inconsistency in the anisotropy or orientation dependence of hardness in the literature for CP-Ti (see Table 2) is further evidence that hardness is a poor choice for calibrating slip resistances.

A few of the Ti nanoindentation studies use the load-displacement curves to estimate microstructure model parameters [21, 27, 28]. However, as demonstrated by the indentation stress-strain analysis, the elastic-plastic transition is not readily apparent on the load-displacement curve [35]. Furthermore, it has been demonstrated that different material properties can produce the same or very similar load-displacement curves [84]. This makes load-displacement curves unreliable for directly estimating model parameters. Indeed, some have included the use of pile-up patterns (height and misorientation profiles) to improve the reliability of model calibrations [21, 22]. It should be seen that the pile-up pattern post-test is only one data point at a very large plastic strain (i.e., the pile-up pattern evolves with plastic deformation). The problem still remains that data critical to the elastic-plastic transition or early stages of plasticity are missing. It should now be even more apparent that the spherical nanoindentation protocols provide this missing information. In addition to the properties listed in

Table 2 and orientation trends presented in this study, the entire indentation stress-strain curve is available for informing the physics-based multiscale models when employing the spherical nanoindentation protocols.

5.3 Limitations of Nanoindentation Datasets for Capturing Plastic Anisotropy of α -Ti

Deformation twinning is an important mode of deformation for CP-Ti, but there is no strong evidence in this work or literature which would suggest it is occurring during nanoindentation (either spherical or Berkovich). It is strongly believed to be a length scale effect; larger indenters are needed to systematically explore deformation twinning in indentation tests. Therefore, there is a critical need to expand the current capabilities of instrumented indentation to larger indenter tip sizes.

Single and polycrystalline samples of Ti show differences in the uniaxial stress-strain response in tension and compression [9, 72]. Presently, there is no clear way to capture this tension-compression asymmetry with indentation. It is also not possible to isolate single slip systems with indentation. However, in this regard, the heterogeneous stresses under the indenter introduce some veracity to the tests since it is a complex stress-state closer to real deformation processes in polycrystalline samples.

Yet another limitation arises from the need to couple the indentation measurements with the corresponding simulations in order to extract or fine tune the model parameters. The contact conditions present in 3-D indentation simulations are a significant challenge to the finite element models currently used in literature. This is particularly exacerbated by the need to employ crystal plasticity constitutive theories in such simulations, which dramatically increases the computational cost involved. In this regard the recent fast computation approaches based on spectral databases offer significant promise [85-87].

6. Conclusions

The following conclusions are drawn from the present study:

1. We have demonstrated for the first time that the spherical nanoindentation stress-strain protocols are capable of capturing the effects of alloying content (chemical composition) in α -Ti, especially in CP-Ti and Ti-64. More specifically, the properties extracted may include indentation modulus, indentation yield strength, indentation initial hardening rate, pop-in indentation stress, and the pop-in size (ratio of the indentation stresses before and after).
2. Spherical nanoindentation protocols are capable of capturing the grain-scale mechanical responses of α -Ti in the form of indentation stress-strain curves, including the initial elastic regime, the elastic-plastic transition, and the early stages of plastic deformation. This information is critical for estimating model parameters needed in physics-based constitutive models.
3. The dataset generated in this study helps clarify the estimates of the elastic constants in literature. Our results support the previous results that indicated α -Ti-64 is more compliant than pure α -Ti. In a similar vein, the results presented here also clarified the yield strength measurements in literature. In particular, it was found that the indentation yield strengths in α -Ti-64 are about 50-80% higher than CP-Ti, with the percentage increases being higher for crystals with the c-axis perpendicular to the indentation direction.

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Tables

Table 1: Nominal chemical compositions of α -Ti and α -Ti-64 based on ASTM and manufacturer's data unless otherwise noted.

Phase	Alloy	O	Al	V	Fe
α -Ti	CP-Ti, grade 2	≤ 0.25	0	0	≤ 0.3
α -Ti-64	Ti-64, grade 5	≤ 0.20	$\sim 7^{[*]}$	$\sim 1^{[*]}$	≤ 0.25

*estimated from literature [44, 45]

Table 2: Orientation dependent elastic and plastic properties from single grain nanoindentation experiments on α -Ti for pure and alloyed (Ti-64) titanium. Indentation measurements come from Berkovich indents using the Oliver-Pharr [31] method unless otherwise noted. Based on the available information, the samples are all very similar in nature (heat treated or annealed) such that prior cold-work has no effect on the indentation results.

Bulk Composition	E_{ind} [GPa]				H or Y_{ind} [GPa]				Maximum Depth (Force) nm (mN)	Ref.
	Near [0001]	Near	Near [1120]	Near [0110]	Near [0001]	Near	Near [1120]	Near [0110]		
	$\Phi=0^\circ$	$\Phi=45^\circ$	$\Phi=90^\circ$	$\Phi=90^\circ$	$\Phi=0^\circ$	$\Phi=45^\circ$	$\Phi=90^\circ$	$\Phi=90^\circ$		
HP Ti (99.999%)	135	136	-	-	1.6	1.9	-	-	2,000	[20]
CP-Ti (grade 1)	159	151	143	143	5.5	4.8	4.4	4.4	1,000	[21]
CP-Ti (grade 2)	-	-	-	-	1	-	0.75	0.75	260-330 (6)	[22]
CP-Ti (grade 2)	130	130	130	130	-	-	-	-	(50)	[23]
CP-Ti (grade 2)*	140	140	140	140	-	-	-	-	(100)	[23]
CP-Ti (na)	-	-	-	-	2.7	2.2	1.3	1.3	(50)	[24]
CP-Ti (grade 2)^	150	130	115	115	1.6	1	0.9	0.9	300	
Ti-7Al	198	-	170	166	7.7	-	5.1	4.6	400	[25]
Ti-64	-	-	-	-	4.3	4.4	4.4	4.2	120-140 (2)	[27]
Ti-64	-	-	-	-	6.3	5	4.5	4.5	300	[29]
Ti-64	-	-	-	-	6.8	5.5	4.8	4.6	300	[26]
Ti-64^	137	115	105	105	2.4	1.9	1.7	1.7	450	
*spherical, 10 μ m radius; ^spherical, 16 μ m radius, nanoindentation stress-strain protocol, present work										

Figure Captions

Figure 1: (a) SEM-BSE micrograph and (b) EBSD inverse pole figure map of CP-Ti. The X marks the same grain in both micrographs for comparison. (c) SEM-BSE micrograph and (d) EBSD inverse pole figure map of Ti-64. The primary- α phase is label (same three grains) in both micrographs. Both samples were electropolished as a final sample preparation step.

Figure 2: Cutout view of the three-dimensional finite element model of the single crystal indenter specimen used in this work.

Figure 3: (a) Load-displacement curves for 16 μm (blue) and 100 (red) μm indents on CP-Ti in the same grain ($g = 175.6, 11.4, 201.1^\circ$), (b) corresponding indentation stress-strain curves with the indentation yield point as filled, colored circles, (c) 16 μm indentation stress-strain curve with the back-extrapolation linear fit of data between the end of the pop-in and a 2% strain offset used to determine indentation yield strength, (d) 100 μm indentation stress-strain curve where the indentation yield point can be determined directly from a 0.2% strain offset.

Figure 4: Indentation modulus (E_{ind}) versus declination angle (Φ) measured from 16 μm radius (blue) and 100 μm radius (red) indenters on CP-Ti. The FE-predicted indentation modulus is determined using single crystal elastic constants from literature [12]. Error bars are $\pm$ one standard deviation which incorporates multiple answers for single tests and multiple measurements in the same grain when applicable. There are approximately 25 grains (35 tests) and 50 grains (74 tests) for the 100 and 16 μm radius indenters respectively.

Figure 5: (a) Indentation yield strength versus declination angle (Φ) for 16 μm radius (blue) and 100 μm (red) radius indents in CP-Ti, (b) the same data in an inverse pole figure (IPF) plot with color scale for indentation yield strength, (c) a surface of indentation yield strength as a function of Bunge-Euler angles (ϕ, ϕ_2) determined from a regression using generalized spherical harmonics (data points are shown as blue dots), and (d) the IPF-contour plot using the surface of indentation yield (data points are filled circles according to their actual values using the same color bar as the surface of indentation yield). The average contact radius at yield for 16 and 100 μm was approximately 500 nm and 2,250 nm respectively.

Figure 6: (a) BSE image of 16 and 100 μm radius indents on CP-Ti in the same grain, (c-d) BSE images of 100 μm radius indents on CP-Ti with crystal lattice orientation shown in the lower left hand corner. The Bunge-Euler angles in degrees for (a-d) are, [59.2, 3.4, 278.1], [59.2, 3.4, 278.1], [166, 42.1, 209.3], and [167.6, 88.2, 206.4], respectively, and the crystal lattice viewed from the surface is also shown in the lower left corner of each micrograph. The inset in (a) is the

indent shown at higher magnification in (b). Slip lines outside the residual indent are drawn for emphasis (white lines) in (c) and (d).

Figure 7: Indentation modulus (E_{ind}) versus declination angle (Φ) measured from 16 μ m radius indenters on α -Ti-64. The FE-predicted indentation moduli (solid and dotted lines) are determined using two different sets of single crystal elastic constants from literature for α -Ti6Al and α -Ti6242 [30]. Error bars are $\pm$ one standard deviation which incorporates multiple answers for single tests and multiple measurements in the same grain when applicable.

Figure 8: (a) Indentation yield strength versus declination with 16 μ m radius indenter on α -Ti in Ti-64 (black) and CP-Ti (blue), (b, c, d) ISS curves with 16 μ m radius indenter for CP-Ti (blue) and α -Ti in Ti-64 (black) for similar orientations spanning the range of declination angle. The solid lines in (a) are from regression analyses. The average contact radius at yield for Ti-64 and CP-Ti was approximately 800 nm and 500 nm, respectively.

Figure 9: Additional indentation stress-strain properties for α -Ti in Ti64 (black) and CP Ti (blue) from 16 μ m radius indenter: (a) indentation hardening rate, (b) pop-in indentation stress, and (c) the ratio of the indentation stress before the pop-in divided by the indentation stress after the pop-in. The solid lines are from regression analyses. The error bars for pop-in plots come solely from the variance in the analysis protocol (i.e., indents in the same grain are plotted as individual data points rather than averaged into a single data point).

On capturing the grain-scale elastic and plastic anisotropy of α -Ti with spherical nanoindentation and electron back-scattered diffraction

Figure 1

Figure 2.

Figure 3

E_{ind} Vs. Declination Angle

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Graphical Abstract