From “smaller is stronger” to “size-independent strength plateau”: towards measuring the ideal strength of iron

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Keywords: ((Ideal strength, Size effect, In-situ TEM, Iron nanoparticle, Strength plateau))

The ideal strength of a metal is the stress at which the lattice itself becomes unstable. This property is of practical interest since it sets an upper bound on the strength of a perfect crystal [1]. However, the effect of crystalline imperfections, e.g. the presence of dislocations, renders the strength of metals far less than their ideal strength [2-5]. A straightforward method to increase the strength of a crystal is to reduce or even eliminate its defects and flaws. This can be achieved through increasing the crystal quality [6-9] or reducing the crystal size [10-13], as revealed by classical experiments on whiskers carried out over half a century ago [7,8] and recent tests on small scale samples [10-13]. Regardless of the methods of how these samples were prepared, the general trend of the size-strength relationship found so far is the same, i.e. “smaller is stronger”. For example, the tensile strength of bcc Fe whiskers exhibited strong strengthening behavior along with decreasing sample diameter [7,8]. Despite of the large scatter in the data, the measured tensile strength increased monotonically to ~ 13.4 GPa when the sample diameter was reduced to ~ 1.6 μm [7]. This stress is very close to the theoretical de-bonding strength of bcc Fe (~ 14.2 GPa) based on density functional theory [14].

Since the measured strength cannot exceed the theoretical strength, based on the trend observed in ref. [7], a size-independent stress plateau should be observed before size-dependent softening [15] begins to take over at room temperature, if we further reduce the sample size. However, no such trend has been reported in past studies. The only exception was for single crystal Mo alloy pillars: Bei et al. [16] found that Mo alloy pillars prepared by chemical etching method yielded without exception at a critical resolved shear stress (τ) of

4.3 GPa for the size regime from 360 nm to 1000 nm. The size-independent strength was ascribed to the pristine nature of as-synthesized samples. By assuming the validity of the rule of mixtures, the shear modulus (G) of as-synthesized Mo alloy was estimated to be 112 GPa [16], about 11% lower than that of pure Mo. Nevertheless, τ is only $\sim 0.038G$, about 3 times lower than the ideal shear strength predicted by theoretical calculations [17]. This indicates that pristine samples are a necessary, but not sufficient condition to achieve ideal strength. Consequently, the following questions are still open for discussion: where is the end of “smaller is stronger” trend in terms of sample size? Can the theoretical strength be measured experimentally in free-standing samples? If yes, how can this be realized?

When materials are subjected to external applied stresses, edges, corners, notches and surface roughness on free surfaces or even atomic-level surface steps can serve as dislocation nucleation sites, at a stress level significantly less than the ideal strength [18-21]. Therefore, in order to experimentally measure the ideal strength in free-standing samples, it is also necessary to suppress surface dislocation nucleation in addition to ensuring pristine internal structure. In principle, a spherical sample with pristine internal structure and passivated smooth surface can be ideal for achieving theoretical strength because of the following reasons. First, the spherical geometry ensures that the maximum stress site is located inside the sample when it is loaded. This is because, based on classical contact mechanics, when two spherical samples are pushed against each other, the maximum stress is located in the interior of the sample instead of at the contact interface [22-24]. Second, the pristine internal structure will eliminate internal sources for defect nucleation. Third, the passivated smooth surface is expected to effectively reduce or even eliminate the possibility of surface dislocation nucleation. It has been reported that surface coating may suppress surface dislocation nucleation effectively [25].

In this letter, we choose spherical single crystal iron nanoparticles to investigate the possibility of experimentally measuring ideal strength in free-standing crystals. These nanoparticles were synthesized by argon plasma evaporation of an iron target, and then passivated in a connecting chamber in an inert gas ambient [26,27]. The size of these particles ranged from tens of nanometers to about 500 nm. Transmission electron microscope (TEM) observations found that all these particles have a thin oxidation layer of 4 nm in thickness, regardless of the particle size, exactly the same as that reported before [26,27]. This suggests that these particles are stable in ambient environment. Most of the iron nanoparticles we used have a spherical shape and therefore the significant effect of faceted surface on deformation reported by Mordehai et al. [28] is not important in our test. In addition, the majority of these particles are free of obvious dislocations and geometric defects although the possibility of small defects cannot be ruled out.

In order to measure the strength of individual particles, the nanoparticles were first individually dispersed on a specially designed Si substrate (Fig. S1) [29]. In situ compression tests were performed in a JEOL-2100F TEM using a Hysitron PI95 PicoIndenter with a flat diamond punch (diameter $\sim 1\ \mu\text{m}$). All the tests were carried out under displacement rate control mode with a constant displacement rate of 5 nm/s. It was found that single crystal iron particles always experience ultrahigh elastic deformation before yielding. One typical example is shown in **Figure 1**. The outer diameter of this particle is about 200 nm, with a 4 nm $\gamma\text{-Fe}_2\text{O}_3$ shell. The corresponding selected area diffraction pattern (SADP) (inset in Figure 1a) of the nanoparticle confirms its single crystalline nature. During compression, symmetrical contrast contours (marked with white arrow in Figure 1b) were observed to form at the contact interfaces and move forward along with the increase of external applied

force until the particle suddenly collapsed (Figures 1b to 1c). Additional details regarding the deformation process are displayed in movie S1. During the collapse, the spherical nanoparticle evolved into a pancake-like plate (Figure 1c). This deformation character is significantly different from the compress of nanosphere Si particles, which only demonstrate gradually local surface damage near the contact point and no such catastrophic failure [30]. The recorded force versus compression ratio (defined as the compression displacement divided by the diameter of the nanoparticle) curve exhibited a near linear relationship up to 30%, followed by a sudden load drop (Figure 1d), indicating ultrahigh elastic deformation before the yielding, in agreement with observation of the microstructural evolution. More compression tests on a smaller (75 nm in diameter) and a larger (410 nm in diameter) iron nanospheres were displayed in Movies S2 and S3, respectively. They all demonstrate similar catastrophic failure feature. In order to confirm the pure elastic deformation before the catastrophic collapse, we unloaded an iron nanoparticle just prior to its plastic yielding and reloaded it to failure. The force vs. compression ratio appears quite linear during the first loading sequence (black dots in Figure 1e) with the maximum compression ratio up to 28%. Because we used the “abort” function to unload, no unloading data were recorded during the first loading sequence. However, it is obvious there is no detectable geometry change before (inset of Figure 1e, original) and after (inset of Figure 1e) the first loading sequence. It is worth noting that there was a small movement of this particle during the unloading process due to the adhesion between the sample and the diamond probe. During the second loading sequence, the force vs. compression ratio curve nearly overlapped with the first until the sample collapsed at $\sim 70 \mu\text{N}$ (Figure 1e, red curve). This suggests that the strain prior to the dramatic collapse is purely elastic. The small discrepancy between the two loading curves as well as the minor contrast difference between the original particle and that after

the 1st loading sequence is mainly due to the slight movement of the particle at the end of the first loading sequence.

The collapse process occurred so fast that we can only capture the final state of the particles (e.g. Figure. 1c). However, it is interesting to note that the thickness of the deformed iron particles is ~ 65 nm (e.g. Figure 1c). This means that the pancake-like iron particles are already a perfect TEM samples and can be easily examined along the thickness direction. In a previous study, we demonstrated that the submicron-sized Au particles can experience “pristine to pristine” deformation [31]. In order to examine if iron nanoparticles had experienced a similar process, a Kleindiek nano-manipulator was used to transfer a pancake-like iron particle onto a 3 mm carbon membrane with its flattened surfaces parallel to the membrane (see Figure S2 for an illustration of the transfer process). As shown in **Figure 2a**, in sharp contrast with that observed in FCC structured Au particles, copious defects are found in the pancake-like iron nanoparticle. The existence of deformation-twinning-like structures (Figures 2b and c) suggests that deformation twinning or local lattice distortion also contributed to the catastrophic plastic evolution. Presumably, this is due to the very high rate of collapse at yielding [32].

In order to reveal the nucleation and evolution of defects in the nanoparticles, which is beyond the capability of existing experimental techniques, molecular dynamics (MD) simulations were employed (the details can be found in the supplementary materials). Single crystal iron spheres with diameter of 30 nm and 60 nm were explored. Regardless of particle size, plenty of defects including dislocations, deformation twins and point defects are observed; they nucleated and interacted with each other and multiplied upon the sudden plastic yielding of the iron particles, leading to the dramatic shape change of the particles in a very short time. Figure 2d is the cross section view of the iron sphere with diameter of 60

nm at the early stage of plastic deformation. Both ordinary dislocation plasticity and deformation twinning are observed to nucleate both from the surface and sample interior and have contributed to the overall plasticity, agreeing well with that observed in laboratory tests.

A total of more than 30 iron nanospheres without obvious flaws were tested in the TEM successfully. Their diameter ranged from 81 nm to 429 nm. In order to check if the maximum stress sustained by these iron spheres can reach the theoretical strength of iron, we have measured the maximum contact pressure (MCP) of each tested nanosphere and plotted the data vs. particle diameter in **Figure 3**. Here MCP is defined as the maximum force sustained by the iron nanosphere prior to the plastic yielding divided by the corresponding contact area, i.e. $\pi d_c^2/4$. Here d_c is the contact diameter corresponding to the maximum force and can be measured directly from the recorded movies. It is worth to point out that Luan et al. [33] had suggested that the continuum contact mechanics will break down when the contact area sinks into nanoscale. However, the contact area in our experiment is much larger than their simulation, especially at the point of collapse, and we also observed stress contours predicted by classical theory. It is also worth pointing out that the nascent defects nucleated in MD simulations corresponded to prediction from classical contact theory as well. Therefore the maximum contact pressure computed from a continuum analysis appears to be appropriate to describe the strength of these materials. At first glance, the MCP data appears quite scattered, which is pretty similar to the scatter of whisker's yield strength summarized and modelled by Sudharshan Phani et al. [34]. In the current experiments, this scatter is largely due to the following three reasons. First of all, it has been well-established that the strength of single crystal iron has a relatively large orientation dependence. In this study, due to the spherical geometry of the tested samples, the loading orientation must

have a distribution, presumably random. Therefore, MCP variation with crystal orientation is expected. Second, even though we have been very careful in carrying out the tests, certain minor misalignments between the samples and the diamond probe as well as the silicon substrate are inevitable. This will also contribute to the scatter of the MCP shown in Figure 3. Third, some defects may be undetectable inside TEM, which can dramatically affected the yield strength of the tested samples. All the aforementioned factors act to scatter the measured MCP, however, they all have the common effect of softening the tested material. In other words, only the highest value found for the MCP of each given sample size represents the condition that is most likely to correspond to the intrinsic strength of the tested samples. Considering these factors, we have purposely highlighted the highest MCP for each sample size in red while all the others in blue, as shown in Figure 3. The data exhibits two obvious size regimes, as marked by the dashed black line. For samples with their diameter larger than ~ 210 nm, the size-strengthening behavior agrees with the well-established tenet of “smaller is stronger”. However, when the sample diameter is below ~ 210 nm, the MCP values (in red color) exhibit a size independent plateau at ~ 10.7 GPa, as marked by the horizontal dashed line. It is worth noting that the value of the critical diameter for transition should be closely related to the sample history which will determine the defects state of the samples [34]. Consequently, the critical value for transition may shift back and forth for samples that were fabricated under different conditions. However, the trend for such transition should be same. Based on classical contact mechanics, the maximum stress experienced by an elastically deformed solid sphere should be at a distance underneath the contact surface [22-24]. Therefore, the actual stress causing yielding should be much higher.

In order to obtain a more quantitative assessment of the critical shear stress for yielding, both finite element model (FEM) and interatomic potential finite element model (IPFEM) were employed to analyze the stress distribution in a 210 nm iron sphere just prior to its sudden collapse. As shown in **Figure 4a**, the standard surface to surface contact is defined, and a fine mesh is used to allow more accurate calculation, the effect of crystallographic orientation was considered in our simulation. The force is applied on the top diamond indenter, and the bottom silicon substrate is fixed. The Young's modulus of the 210 nm iron sphere is determined to be about 221 GPa by adjusting the simulated force vs. displacement curve to overlap with that measured experimentally (Figure 4b). This value is the isotropic modulus and just in the range of the Young's modulus of bulk single crystal iron, i.e. from 129 GPa to 276 GPa, depending on the crystal orientation. One limitation of our FEM is that it can only model linear elastic problems. However, when the external applied stress approaches the theoretical stress of the material, nonlinear elastic deformation has to be considered and anisotropic elasticity must be used to accurately capture stress distributions. We therefore also adopted IPFEM to tackle the nonlinear anisotropic elastic deformation of the 210 nm iron sphere and compressed along <001> orientation. Similar to the stress contour contrast observed during in-situ compression test shown in Figure 1b and Movie S1, the cross sectional view of the maximum von Mises stress exhibits an arc band profile, as shown in Figure 4c. According to the IPFEM calculation, the corresponding local maximum shear stress on [11-1](101), [11-1](123) and [11-1](112) are 9.4 GPa, 12.4 GPa and 12.8 GPa, respectively.

We now compare this stress level with the prediction given by the Frenkel shear model [35], which gives an estimate of the ideal shear strength of a metal as

$$\tau^{ideal} = \frac{Gd_{uvw}}{2\pi d_{hkl}} \quad (1)$$

Where d_{uvw} is the lattice spacing of the shear direction, and d_{hkl} is the lattice spacing of the shear plane, and G is the shear modulus. For BCC single crystal iron, if we use $G=65$ GPa as the shear modulus of single crystal iron along the $\langle 111 \rangle$ direction [36], the ideal shear strength is estimated to be 8.45 GPa, 14.6 GPa and 22.4 GPa for shear along $[11-1](101)$, $[11-1](123)$ and $[11-1](112)$, respectively. As shown above, our experimental measured data indicate a shear strength of ~ 9.4 GPa for $[11-1](101)$ shear. This magnitude is very close to the estimated ideal shear strength of iron by the Frenkel model above and density function theory calculation [37]. In other words, under the triaxial stress loading condition (possible confined pressure effect) and the confinement by the oxide layer in our tests [22-24,38,39], the upper bound of experimentally measured critical shear stress for yielding indeed close to the theoretical shear strength of iron.

In summary, our work reveals that the ideal strength can be achieved in the spherical iron nanoparticles with an almost dislocation-free interior. Using quantitative compression in a TEM, we have demonstrated that, when the diameter of iron nanospheres is less than 210 nm or so, the contact pressure saturates at 10.7 GPa, no longer following the usual “smaller is stronger” trend. Structural catastrophic collapse is observed to set in suddenly upon yielding. Microstructural observations and MD simulation found that ordinary dislocation slip and deformation twinning are the dominating plastic deformation mechanisms. Further FEM and IPFEM analysis suggest that the experimentally measured loading pressure/stress plateau corresponds to a maximum shear stress of ~ 9.4 GPa, which is very close to the theoretical shear strength of iron for the slip along $[11-1](101)$.

Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the grants from NSFC (51231005, 51471128, 11132006 and 51321003) and 973 Program of China (2012CB619402). We also appreciate the support from the 111 Project of China (B06025). W.Z.H was supported by the new faculty start-up funding from XJTU. Both E.M. and J.L. carried out this work under an adjunct professorship at XJTU. J.L. acknowledges support by NSF DMR-1120901 and DMR-1240933. S.O. and H.K. acknowledge support by ESISM.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figure 1

Figure 1. A typical in-situ compression test of an individual spherical iron nanoparticle. (a)-(c) Extracted video frames of the in-situ compression test of a spherical iron nanoparticles with the diameter of 200 nm. (a) to (b) are taken at the point marked on the force vs. compression strain curves shown in (d). (e) The cyclic loading curves of a spherical iron nanoparticles with diameter of 132 nm and the corresponding dark field TEM images before compression, after first loading and after collapsing.

Figure 2

Figure 2. (a) TEM image of an iron nanoparticle after plastic deformation viewed along the loading direction. (b) HR-TEM image of a shear band formed during catastrophic collapsing where multiple deformation twins-like structures are found. The inset shows a FFT pattern of this region. (c) A Fourier-filtered image from the region marked by the white box in (b). (d) MD simulations reveal ordinary dislocation slip and deformation twinning in the deforming iron nanoparticle.

Figure 3

Figure 3. The measured maximum contact pressure as a function of the diameter of spherical iron nanoparticles. A clear size-dependent behavior is found for nanoparticles larger than 210 nm, and a size-independent strength plateau is observed for nanoparticles smaller than 210 nm. The dash line is added for legibility only.

Figure 4

Figure 4.(a) The simulation geometry of a compression test of a spherical iron nanoparticle in FEM and IPFEM; (b) The estimate of the Young's modulus of an iron spheres with a diameter of 210 nm by using the FEM through direct comparison of the force vs. displacement curves; (c) Projection of stress on the x-y plane of the crystal. The color distribution represents the distribution of von Mises stress.

The table of contents

The trend from “smaller is stronger” to “size-independent strength plateau” is observed in the compression of spherical iron nanoparticles. When the diameter of iron nanospheres is less than a critical value, the maximum contact pressure saturates at 10.7 GPa, corresponds to a local shear stress of ~ 9.4 GPa, which is comparable to the theoretical shear strength of iron.

Keywords: ((Ideal strength, Size effect, In-situ TEM, Iron nanoparticle, Finite element model))

Title ((From “smaller is stronger” to “size-independent strength plateau”: towards measuring the ideal strength of iron))

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ToC Figure

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.((201500377))

From “smaller is stronger” to “size-independent strength plateau”: towards measuring the ideal strength of iron

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Simulation methods

Figure S1-S3

Movie S1-S3

Simulation methods

The EAM potential parameterized by Mendelev [1] is used to describe the interatomic interactions of iron atoms. Three different diameter iron sphere were modeled: 15 nm, 30 nm and 60 nm. All nanoparticles are first relaxed by molecular dynamics simulations and then compressed between two planar indenters. One of the indenters moves toward the particle with a constant velocity and the strain rate is $\sim 10^8 \text{ s}^{-1}$, while the other indenter is fixed. The interaction between the indenters and the iron atoms is described by a repulsive potential. The iron nanoparticles were loaded in two close crystal directions [100] and [511], which are selected based on observed experimental observations. We examined the deformation process of the nanoparticles at both room temperature (300K) and low temperature (25K). During compression, both isothermal (using a Nose-Hoover thermostat) and adiabatic conditions were used to examine the temperature rise and its effect on the corresponding deformation processes.

Finite element analysis was conducted in ANSYS150. The finite element model comprises three parts. The top (Diamond tip) and bottom (Silicon substrate) parts are modeled as blocks meshed by SOLID185, and the middle is a sphere made of iron, covered by a layer of $\gamma\text{-Fe}_2\text{O}_3$ shell with thickness 4 nm. This part is meshed by SOLID187. Two contact pairs were created to simulate the contact between the sphere and two blocks, respectively. Due to geometric symmetry, one quarter was modeled. The bottom surface of the silicon substrate is fixed. A displacement loading was applied on the diamond tip. The reaction forces were obtained to compare with the experimental data.

In addition, using the interatomic potential finite element method (IPFEM) [2,3], we performed three-dimensional simulations of compression tests on iron nanospheres while taking into account the nonlinear anisotropic elastic effects on large deformation of single-crystal iron. Within the framework of the embedded-atom method (EAM) [4], the interatomic potential-based hyperelastic model for the body-centered cubic crystal of iron was implemented in the finite element program ABAQUS/Explicit (2011) [5] by writing a user-material subroutine called VUMAT. The EAM potential of iron developed by Mendelev *et al.* [1] was used in this study. The diamond tip and Si substrate were modeled as rectangular slabs of isotropic linear elastic materials (i.e., Young's modulus and Poisson's ratio are 1220 GPa and 0.20 for diamond and 185 GPa and 0.28 for Si, respectively). Since

this analysis was focused on the deformation behavior inside the bulk crystal of iron, the effects of nonlinear elasticity of diamond tip and Si substrate were ignored.

The iron nanosphere with a diameter of 210 nm (D) and the slabs with the in-plane size of $1.2D \times 0.6D$ and depth of $0.2D$ were employed, so that the number of elements in a sphere was 25,757 and that in a diamond/Si slab was 1152. This D value is sufficiently larger than effective range of atomic interactions in a homogeneous iron crystal, and thus considered to be large enough to employ the local continuum approximation. In the dynamic, explicit computational procedures of this program, the nonlinear response was obtained incrementally. The boundary conditions were imposed as follows: the displacement along the bottom of the Si mesh was constrained to be zero, while the displacements of lateral surfaces were unconstrained. The diamond slab was moved down in displacement control at a sufficiently low rate to mimic the quasi-static loading condition. The iron nanosphere was pressed along the [001], [110] and [111] directions in IPFEM simulations.

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Figure S1

Figure S1. Schematic drawing of the set-up for the in-situ compression test of individual iron nanoparticles. The nanoparticles were dispersed on a wedged Si substrate for compression testing in the TEM. In order to observe the microstructure evolution of the nanoparticle under the electron beam and ensure the diamond tip accessed easily, the wedged Si substrate was fixed on the Cu mount in the TEM holder normal to the electron beam. Then, the flat diamond tip was brought into contact with the iron nanoparticle while it was being observed. The diamond tip was coarsely positioned using manual screws, and then finely positioned in the x, y and z directions using a piezoceramics actuator. The iron nanoparticle was compressed between the flat diamond tip and the Si substrate and the deformation behavior was simultaneously observed in the TEM using a real-time recording system. The displacement control mode was used, and the rate was 5 nm/s.

Figure S2

Figure S2. Extraction process of compressed pancake-like iron nanoparticle in FIB chamber by using nano-manipulator.

Figure S3

Figure S3. Bright-field TEM images of the iron nanoparticle with diameter of 429 nm before (a) and after (b) the compression test. Lots of defects were observed in the thinned iron pancake from bright-field TEM image (c) and dark-field TEM image (d).