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Size-dependent plasticity in micron- and submicron-sized ionic crystals

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Uniaxial microcompression methodology is applied to study mechanical behavior of <100>-oriented NaCl, KCl, LiF and MgO single-crystal pillars ranging from 250 nm to 4 µm in diameter. As in metallic materials a strong size effect with regard to compressive strength is observed, NaCl, KCl, LiF and MgO pillars exhibit scaling exponents of -0.64 ± 0.02, -0.72 ± 0.02, -0.68 ± 0.02 and -0.8 ± 0.03, respectively. These compare well to face centered cubic (fcc) metals, but the normalized stress levels of LiF and MgO are higher than those of NaCl, KCl and fcc metals. The differences in strength levels are interpreted in terms of the susceptibility to ion induced damage, which is intrinsic to the fabrication process. In addition, the strong size-dependent plasticity of <100>-oriented ionic crystals can be correlated with their lower critical temperatures.

Keywords: Compression; Ionic crystals; Mechanical properties; Ion irradiation; Size effects

1. Introduction

Significant advances have been made in applying uniaxial microcompression methodology [1] to study mechanical behavior of small-sized materials (i.e. from a few microns to about 100 nm). It is well established that yield stress ($\sigma_y$) scales inversely with sample dimension ($d$) in metals, by a relationship of $\sigma_y \propto d^m$ [2-5], where $m$ is the size-effect exponent. Fcc metals (e.g. Ni [1], Au [6], Al [7], Cu [8]) show strong and relatively constant size dependence with $m$ of -0.6 to -0.7 [2, 5, 9], but in bcc metals less pronounced and inconstant size-effect exponents of -0.20 to -0.5 and of -0.4 to -0.9 were found in Nb, Ta, Mo and W by Schneider et al. [10, 11] and Kim et al. [12, 13], respectively. To date the studies on size-dependent plasticity have mostly been performed on metallic systems.
Ionic crystals (e.g. NaCl, KCl, LiF and MgO) in single-crystal forms are normally highly pure and with low dislocation densities (less than $10^9$ m$^{-2}$) [14]. One of the simplest forms among ionic crystals is the rocksalt (NaCl) structure. Normally ionic crystals have two types of slip systems: soft slip systems with {110} slip planes and Burgers vectors of $\frac{1}{2} <110>$ and hard slip systems with {100} slip planes and Burgers vectors of $\frac{1}{2} <110>$. For example, at room temperature, the soft slip systems ({110} $<110>$) of NaCl and KCl have critical resolved shear stresses (CRSS) of approximately 1 MPa and 0.5 MPa, respectively, while their hard systems ({100} $<110>$) have CRSS of approximately 7 MPa and 2 MPa, respectively[15]. Ionic crystal has been used as a testing ground for dislocations and plasticity since the 1930s and has been thoroughly investigated [15, 16]. This is the starting point of the current study on size-related phenomena.

The first study of size-related phenomena in ionic crystals was reported by Nadgorny et al. [14], who observed similar plastic flows and size-effect exponents in both as-grown and $\gamma$-irradiated LiF micropillars. Recently, Korte and Clegg [17] and Soler et al. [18] found that, in MgO and LiF respectively, the size-related plasticity was also dependent on crystal orientations: The micropillars deformed on soft slip systems exhibited a stronger size effect than the ones deformed on hard slip systems. However, understanding of the size effect in ionic crystals is far from mature, and systematic experimental studies on small-sized ionic crystals are scarce. To the authors’ knowledge, microcompression tests of NaCl and KCl, which have been serving as good examples of ionic crystals, have not been reported so far. In addition, the lower limit of pillar diameter in previous studies on ionic crystals was 0.5 μm. This paper constitutes a study on the mechanical behavior of $<100>$-orientated NaCl, KCl, LiF and MgO pillars in the diameter ranging from a few microns to about 200 nm.
2. Experimental methods

Micron- and submicron-sized pillars were prepared from bulk pure NaCl, KCl, LiF and MgO single crystals (CrysTec GmbH, Germany) with <100> direction normal to surface planes using focused ion beam (FIB) technique (Helios Nanolab 600i, FEI). To avoid the charging problem, a 5 nm thick gold layer was deposited before FIB milling. A two-step milling method using different beam currents was applied to produce cylindrical pillars: 2.5 nA for coarse milling and 40-80 pA for fine milling. The pillars produced were in the diameters of approximately 4 µm, 2 µm, 1 µm, 500 nm and 250 nm, and an aspect ratio of 2.5-4. A taper of 2-3° was generally observed for these pillars, and the top diameters were chosen to calculate stresses. At least 4 pillars of each size were compressed using a nanoindenter (Triboindenter, Hysitron Inc., USA) with a flat diamond punch tip (5 µm in diameter, Synton, Switzerland) under displacement control mode by feedback mechanism. The displacement and loading time were changed according to the pillar height in order to keep a constant strain rate. A strain rate of $2.2 \times 10^{-3} \text{s}^{-1}$ was used for all compression tests. The morphologies of the pillars were characterized using scanning electron microscopy (SEM) before and after compression. It should be noted that NaCl and KCl are hygroscopic, so all the samples had to be stored in an exsiccator before and after tests.

3. Results

Engineering stress-strain curves for the compressed NaCl, KCl, LiF and MgO pillars with different diameters ranging from 4 µm to 250 nm are shown in Figure 1 (a), (c), (e) and (g), respectively. It is observed that the smaller pillars have higher yield and flow stresses than the bigger pillars. For example, 250-nm NaCl pillars have yield stress (measured as offset flow stress at 0.2% of strain) of $\sim 0.25-0.35 \text{GPa}$, which is $\sim \times 5-7$ of
that of 4-µm NaCl pillar (~0.05 GPa) and ~×250-350 of that of bulk NaCl single crystal (~1 MPa) [15, 19]. Moreover, displacement bursts generally occurred in both big and small pillars, showing a similar phenomenon to what has been found in fcc and bcc metals [20, 21]. Due to displacement bursts, both the stress of the pillars and the lateral friction can be released, which may affect the strain hardening rate. Some of the stress-strain curves exhibit nonlinear part at the initial stage of compression, as shown in the curve for MgO in Figure 1 (g), which could be due to the misalignment between the flat punch and the top surface of the sample [2]. To reduce the influence of the displacement bursts on analysis, the highest stress value measured below 5% strain is defined as flow stress $\sigma_{0.05}$. The relationships between $\sigma_{0.05}$ and the pillar diameter for NaCl, KCl, LiF and MgO are plotted in Figure 1 (b), (d), (f) and (h), respectively.

As shown in the compressed pillars in Figure 2, discrete slip bands are observed along the gage length of the samples, showing either one or two localized slip bands on the deformed pillars. Both single and multiple slip is observed in the pillar samples. Those slip bands traverse the entire cross sections of each sample, and multiple slips are always observed for the samples that experienced large strains, as shown in the 4-µm NaCl pillar. Multiple slip is expected to contribute to strain hardening. No wavy morphologies as those observed in W and Mo pillars [10, 11] are found in the ionic crystals. The slip bands are oriented at approximately 45° from the loading axis (<100>-direction), indicating that all pillars were deformed by crystallographic slip on {110}-type planes along <110>-type directions, which are the same as the soft slip systems in their bulk forms. As shown in Figure 2, a bigger taper and some degrees of bending are observed in the smallest pillars, although not always. This bigger tapering could lead to localized plastic deformation on the top area of the pillar and also higher effective stress values. The bending of the pillars could be introduced by misalignment between the
pillar and punch, leading to a reduction in the measured modulus and stress [22-24]. It should be also noted that in the FIB-milled NaCl and KCl trenches a large number of small crystals grew around the FIB-milled pillars. They might be caused by the FIB-milled NaCl and KCl surfaces absorbing water in air, but they were too small to be contacted by the flat punch during compression and did not influence the results of measurement.

4. Discussion

By compression along <100> direction, four equivalent slip systems with a Schmid factor of 0.5 can be activated. Because it is difficult to judge yield strength here, \( \sigma_{0.05} \) is used to give a quantitative analysis. The highest \( \sigma_{0.05} \) of NaCl observed in this study is 0.4 GPa (as shown in Figure 1(b)), so its resolved shear strength is 0.2 GPa, which corresponds to a normalized shear strength of \( G_{\text{NaCl}(110)/90} \) \( G_{\text{LiF}(110)/60} \) and \( G_{\text{MgO}(110)/32} \), respectively, where the shear modulus can be calculated using elastic constants from reference [25] As the theoretical strength is in the range of \( G/30-G/2\pi[26] \), the plastic deformation in NaCl and KCl pillars is expected to be controlled by both dislocation nucleation and propagation. The values for LiF and MgO, however, approach their theoretical strengths.

The difference of the normalized stresses between these ionic crystals could be caused by various defect densities induced by irradiation damage during the FIB milling process. Although LiF, NaCl and KCl are all alkali halides, the defect formation energy of LiF is ~3-5 times higher than those of NaCl and KCl [27, 28]. Thus, LiF pillars may have lower defect densities than NaCl and KCl pillars after FIB milling. Similarly, despite having the identical crystal structure, MgO is much less susceptible to radiation
damage than alkali halides [29]. Consequently, the lower defect densities in FIB-milled LiF and MgO could lead to higher strengths, even close to the theoretical values.

Dou and Derby [9] analyzed the microcompression data of single crystal Au, Al, Ni and Cu pillars by a power-law fit in the form of $\sigma/G = A(D/b)^m$, where $\sigma$ is the resolved shear stress on the appropriate slip system, $G$ is the shear modulus of corresponding slip system, $A$ is a constant, $D$ is the pillar diameter, $b$ is the Burgers vector and $m$ is the size-effect exponent. We applied this power law to fit the data of $<100>$-orientated NaCl, KCl, LiF and MgO pillars in this study, LiF [14, 18] and MgO [17] as reported, fcc metals (Au [6, 30], Ni [31], Al and Cu [32]) and bcc metals (Nb, Ta, Mo and W [10, 11]), as shown in Figure 3. In order to make a comparison, the curves published in the literature were re-evaluated, and resolved shear stresses at 5% strain are used for both the samples in this study and the data from literature. Figure 3 (a) indicates that $<100>$-orientated NaCl, KCl, LiF and MgO exhibit size-effect exponents of -0.64 ± 0.02, -0.72 ± 0.02, -0.68 ± 0.02 and -0.8 ± 0.03, respectively, and the exponents for LiF and MgO in this study are close to those reported in literatures [14, 17]. Moreover, the absolute normalized strength levels for NaCl and KCl are similar, but the ones for LiF and MgO are significantly higher. This difference in normalized stresses might be due to the lower FIB-induced defect densities in LiF and MgO pillars, as indicated above. Interestingly, the hard slip systems ($\{100\} <110>$) of MgO measured by Korte and Clegg [17] and LiF measured by Soler et al. [18] show much weaker size effects than the ones deformed on the soft slip systems in this study. It is observed that the normalized strengths of MgO and LiF deformed on the soft slip systems in this study can even surpass those deformed on the hard slip systems in the studies of [17] and [18]. However, as both hard and soft systems are expected to converge to the theoretical values in the same magnitude, we attribute this effect to a
lower initial or FIB-induced dislocation densities in MgO and LiF in this study compared to [17] and [18].

Figure 3 (b) pinpoints the similarities in normalized strength levels between fcc metals and ionic crystals. It seems that the difference in slip systems does not play an essential role in the size-effect exponents between fcc metals and ionic crystals. Figure 3 (c) compares ionic crystals to bcc metals (i.e. W, Mo, Ta and Nb) as reported by Schneider et al. [10]. Unlike ionic crystals and fcc metals, they exhibit various size-effect exponents ranging from -0.43 to -0.93 [10]..

Schneider et al. [10] correlated the size dependence of several bcc metals to their critical temperatures and found that the size-effect exponent scales inversely with the critical temperature. Here, the critical temperature is defined as the temperature above which the flow stress becomes insensitive to the test temperature. When the test temperature is close to the critical temperature, the mobility of screw dislocations is close to that of edge dislocations, and the size-effect exponents of bcc metals approach those of fcc metals. Here, we plot the power-law exponents of ionic crystals and bcc metals as a function of test temperature over the critical temperature [10, 15], as shown in Figure 3 (d). The critical temperatures of ionic crystals in this study are obtained from stress-temperature curves measured in [15]. It shows the ionic crystals follow this pattern well. Those deformed on \{110\} <110> slip systems have low critical temperatures (generally below 100 K [15]). Thus, they exhibit almost uniform size-effect exponent around -0.7. Those deformed on \{100\} <110> systems have higher critical temperatures (~1200 K for MgO [15] and ~500 K for LiF [33]) and they have much smaller, and even no, size dependence of plasticity.
4. Conclusions

The microcompression technique was applied to study the mechanical behavior of FIB-milled <100>-orientated NaCl, KCl, LiF and MgO single crystals at micron- and submicron scales. The results show that the size-effect exponents of these <100>-orientated ionic crystals are similar to fcc metals. A variation in normalized strengths for these ionic crystals might be attributed to different defect densities induced by FIB milling. The size dependence correlated with critical temperature can be used to compare ionic crystals to fcc and bcc metals.

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References

Figure captions

Figure 1. Representative engineering stress-strain curves for <100>-oriented single crystals: (a) NaCl, (c) KCl, (e) LiF and (g) MgO pillars with the diameters ranging from 4 µm to 250 nm; the corresponding engineering stress at 5% strain ($\sigma_{0.05}$) as a function of the pillar diameter: (b) NaCl, (d) KCl, (f) LiF and (h) MgO.

Figure 2. SEM images of representative NaCl, KCl, LiF and MgO pillars: as FIB-milled (the top row) and compressed (the bottom row). The loading direction is along the surface normal axis of <100>, the slip bands caused by {110} <110> slip systems are schematically illustrated.

Figure 3. Resolved shear stress at 5% strain normalized by the shear modulus $G$ on corresponding slip system versus the diameters normalized by the Burgers vector $b$ for FIB-milled (a) ionic crystals, i.e. NaCl, KCl, LiF, and MgO in this study and ref [14, 17, 18], (b) with fcc metals (i.e. Au, Ni, Al and Cu [6, 30-32]) and (c) bcc metals (i.e. Nb, Mo, Ta, W [10]) and (d) the relationship between the size-effect exponents and the test temperature normalized by the critical temperatures.
Figure 1
Figure 2
Figure 3