Microstructural evolution of a focused ion beam fabricated Mg nanopillar at high temperatures: Defect annihilation and sublimation

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Microstructural evolution of focused ion beam machined Mg nanopillars was investigated by in situ heating experiments in a transmission electron microscope. The dislocation loops generated by a Ga⁺ ion beam were annihilated at around half of the melting point of Mg. At a higher temperature (673 K), the sublimation of Mg occurred due to the reduced stability of Mg under the vacuum environment. In the course of sublimation, the Ga-rich liquid was formed and stabilized the structural instability of moving solid–vapor interface.

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In recent years, the deformation behaviors of sub-micro/nano scale materials have been intensively investigated, mostly driven by the occurrence of novel mechanical properties not observed in bulk materials [1]. Most of experiments involved the use of a focused ion beam (FIB), which allows machining of a material into the desired geometry for mechanical testing [2,3]. Although FIB machining became a key technology in small-scale mechanics, its side effects raise serious concerns about the validity of mechanical data. When the Ga⁺ ion beam impacts the specimen surface during a FIB imaging or milling process, structural defects such as point defects and dislocation loops, or even amorphization are induced in the surface region due to the knock-on displacement and/or Ga⁺ implantation [4]. Among these defects, the dislocations are not ignorable in density and already known to significantly affect the mechanical properties [5]. Recently, Hütsch and Lilleodden [6] demonstrated that the stress–strain responses of Mg pillars are dramatically modified with the change of FIB milling conditions.

The effect of Ga implantation is not limited to mechanical properties, but can also change the physical properties and the thermodynamic stability. In the case of Mg, a small addition of Ga near the surface region can cause the formation of Mg–Ga intermetallic phases or a decrease of the melting point ($T_m$, 923 K) due to the extremely low melting point of Ga (303 K) [7]. At the nanometer scales, the Ga-induced effects can be more pronounced since the relative portion of Ga implanted volume increases and a capillary effect might come into play with an increase of local curvature.
In this study, we have carried out in situ TEM heating experiments of Mg nanopillars prepared by FIB. The objective is to investigate the thermal behavior of structural defects, dislocations in particular, upon annealing, and how the implanted Ga affects the thermal stability of Mg in the nanoscale dimension.

Using a FIB workstation (Quanta 3D FEG, FEI), a thin slice was cut from a pure single crystal Mg (99.999%, Goodfellow) and attached to a Cu grid by Pt deposition. A cylindrical pillar with a diameter of 300 nm was machined using a 30 kV Ga\(^+\) ion beam at annular milling mode with a final milling current of 10 pA. In situ heating experiment was carried out in a transmission electron microscope (TEM; JEOL 2100F; JEOL) operated at 200 kV and under a column base pressure of \(\sim 1 \times 10^{-10}\) bar. The sample was first heated from 298 K to 393 K in 20 min. From 393 K, temperature was increased in 10 K steps after stabilizing for 10 min at each temperature. Real-time movies were recorded using a charge-coupled device (CCD) camera (ORIUS 200D, Gatan). Electron energy loss spectroscopy (EELS) was carried out to characterize the chemical composition of the pillar after the heating experiment using an aberration-corrected TEM (JEOL 2200FS) operated at 200 kV.

The microstructure of the as-prepared Mg pillar is shown in Fig. 1(a). Small dislocation loops (white arrow) are one of the structural defects generated by the high energy Ga\(^+\) ion beam [8–10]. These loops are most likely an interstitial type, similar to what observed by Idrissi et al. from Al [9]. The short segments of dislocations in a pile-up array (black arrow) are preexisting dislocations that were already present in the bulk Mg crystal (or introduced by plastic deformation of the pillar during handling), and the dark region at the top is the residue of a Pt protection layer.

When the Mg pillar was heated in the TEM, dislocations were annihilated progressively, leaving the pillar free of dislocations. The annihilation of dislocation loops was accelerated when the temperature reached 433 K (Supplementary Movie 1; Fig. 1(b)), a temperature close to half of the \(T_m\) of Mg. The annihilation of dislocation loops can be explained by a vacancy-assisted diffusion process [11]. The equilibrium vacancy concentration, calculated using the enthalpy of vacancy formation of 0.88 eV for Mg [12], is \(\sim 10^{10}\) cm\(^{-3}\) at 433 K and \(\sim 10^{15}\) cm\(^{-3}\) at 298 K. Driven by a concentration gradient, the proliferated vacancies diffuse toward the interstitial-type dislocation loops. The present result demonstrates that a post-annealing process at around half of \(T_m\) is quite effective to eliminate the structural defects formed in a metal pillar produced by high energy Ga\(^+\) ion beam. Similar behaviors were also observed in other metals as well [8,10,13].

Different from the dislocation loops, the preexisting dislocations were annihilated at a higher temperature (\(\sim 673\) K; \(T/T_m \sim 0.7\)) by glide and subsequent escape through the surface (Supplementary Movie 2; Fig. 1(c)). One should note that the annealing resulted in the surface oxidation and contamination (mostly carbon) of the Mg pillar. The surface Mg-oxide, however, was not rigid enough to block the escape of dislocations.

While the dislocations were all annihilated at around 673 K, the movement of a boundary was observed to start from the bottom mount of the pillar to the top end (Supplementary Movie 3; Fig. 1(c)–(e)). In Fig. 1(d), the lower part swept by the boundary is considered as vacuum as its diffraction intensity is comparable to the vacuum level, whereas the upper region remains as solid. The movement of the boundary, therefore, is the consequence of sublimation of Mg. The sublimation left behind an empty cylinder (Fig. 1(e)) after the gas phase of Mg escaped the cylinder through the open surface at the lower part of the pillar. Detailed EELS elemental mapping near a cylinder edge (Fig. 1(f)) showed that the cylinder is comprised of two layers, a carbon-rich inner layer and a Mg-oxide outer layer (Fig. 1(g)). These layers had formed and thickened on the surface of the Mg pillar to \(\sim 30\) nm.

Fig. 1(h) shows the plot of the height (\(h\)) variation of the remaining solid Mg (Fig. 1(d)) as a function of time (\(t\)) at 673 K. The fact that the data points lie on a straight line indicates that the moving rate of the boundary is constant throughout the sublimation. This behavior is described well by the Hertz–Knudsen equation which dictates the evaporation rate (\(\Gamma\)) of a condensed phase [14].

\[
\Gamma = \frac{n}{A_d} \frac{dN_e}{dt} = v_e \left( \frac{m}{2nk_B T} \right)^{1/2} (P^0 - P)
\]  

(1)

\(n\): number density of Mg atoms, \(A_d\): apparent area of the boundary, \(dN_e\): number change of Mg atoms, \(v_e\): evaporation velocity of Mg atoms, \(m\): mass of Mg atom, \(k_B\): Boltzmann constant, \(T\): temperature, \(P^0\): saturated vapor pressure, \(P\): ambient pressure.
where $m$ is the molar mass, $A_r$ the area of evaporating surface, $N_e$ the number of evaporating atoms, $k_B$ the Boltzmann constant, $T$ temperature, $P^0$ the equilibrium vapor pressure, and $P$ the pressure acting on the evaporating surface. Assuming a cylindrical shape of pillar, the equation can be expressed in terms of the time derivative of the pillar height ($h$) as:

$$\frac{dh}{dt} = -\gamma \Omega \left( \frac{1}{2\pi mk_B T} \right)^{1/2} (P^0 - P)$$

(2)

where $\Omega$ is the molar volume. For simplicity of calculation, we assumed $\gamma$ as a unity and $P$ as the value corresponding to the TEM column pressure ($\sim 10^{-10}$ bar) (even though the local $P$ value close to the boundary might be different). From the slope of the $h$ vs. $t$ plot in Fig. 1(h), $P^0$ is calculated to $5.326 \times 10^{-7}$ bar. In principle, the sublimation is thermodynamically preferred once the equilibrium vapor pressure $P^0$ is larger than the TEM column pressure ($P \sim 10^{-10}$ bar), i.e. $P - P^0 < 0$. The calculated $P^0$ is $10^3$ times higher than the TEM column pressure. Because of the large driving force, the sublimation of whole pillar was completed in a relatively short time (less than 1 min).

The morphological evolution of the moving solid–vapor interface is shown in Fig. 2(a) through (e) (Supplementary Movie 3). The solid–vapor interface is distinguished by its morphologies, one characterized by the flat morphology (Fig. 2(b)–(d)) and the other with a cusp at the triple junction (Fig. 2(e)). The flat interface was inclined instantaneously in the course of the sublimation (Fig. 2(a)), but it became straightened soon (Fig. 2(b)). The driving force that leads to straightening of the interface on its motion is the lowering of total interface energy ($\gamma_{SV}$) by reducing the interface area, and also the relaxation of imbalance between the interface tension components along the direction of motion. However, as shown in Fig. 2(b)–(d), the persistent sublimation with maintaining a flat solid–vapor interface meets an instability condition; the diffraction contrast of the solid Mg fluctuates repeatedly just before the formation of the cusp at the triple junction (Supplementary Movie 3). Once the cusp forms, the Mg solid exhibits uniform diffraction contrast (Fig. 2(e)) which remains unaltered in the course of remaining sublimation. Thus, it appears that the transition from the flat to the cusped interface morphology relieves a structural instability imposed on the solid Mg. Afterwards, the volume of liquid cusp increases continuously until the whole Mg had been sublimated.

In order to understand the observed thermal behaviors, one has to consider the effects of pressure and also the implanted Ga in Mg. As shown in Fig. 3, the Mg–Ga binary phase diagram was calculated by employing a CALPHAD-type approach with taking account of the TEM column pressure ($\sim 10^{-10}$ bar) [15,16]. While the Ga-rich liquid phase remains stable under $10^{-10}$ bar, the Mg-rich liquid phase is not predicted to exist stable at all. Over a wide range of Ga composition ($\sim 70\%$) the sublimation temperature of Mg–Ga solid phases varies in a stepwise fashion and remains lower than 673 K. Therefore, for pure Mg and also for other Mg-rich solid phases the direct sublimation is thermodynamically favored at 673 K under $10^{-10}$ bar. Except pure Mg gas, Ga-rich liquid is the only stable phase at 673 K as indicated by the red-dotted line in Fig. 3.

As the sublimation of Mg proceeds, the solid–vapor interface becomes gradually enriched by Ga due to the out-diffusion of implanted Ga from the surface of pillar. According to the calculated phase diagram, the increasing quantity of liquid phase at the triple junction with the sublimation can be understood as a result of the Ga enrichment (Supplementary Movie 3). Note that the Ga-rich liquid phase, compared to the solid Mg, exhibits darker amplitude contrast in the TEM images due to the higher atomic scattering factor of Ga (Fig. 2(e) and Fig. 4(c)).

The Ga-rich liquid phase is preferred to nucleate at the triple junction of the moving solid–vapor interface because of the highest local Ga concentration. More importantly, the liquid phase can relieve any imbalance between the interface tensions at the triple junction as it can immediately adapt its shape. One should note that the solid–vapor interface tension, if the interface is straight, has only the tangential component acting along the plane of the interface (denoted by $\gamma_{SV}$ in Fig. 4(a)). This interface tension remains unbalanced during the

![Fig. 2. TEM images showing the morphological evolution of the solid-vapor interface during the sublimation of Mg nanopillar at 673 K (Supplementary Movie 3). (a) The inclined solid-vapor interface. (b)–(d) The straight interface with exhibiting a fluctuation in the diffraction contrast of Mg. (e) A formation of Ga-rich liquid cusp at the triple junction.](image)

![Fig. 3. Calculated phase diagram of the Mg–Ga binary system under the pressure of $10^{-10}$ bar. The temperature corresponding to the present study is indicated by a red-dotted line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)
Ga\textsuperscript{+} ion beam can be eliminated by annealing at round half of $T_{lv}$.

The sublimation of Mg initiated and proceeded at 673 K in the vacuum environment of the TEM because of the lowered thermal stability of Mg, i.e., the high equilibrium vapor pressure. During the sublimation, the morphology of the moving solid–vapor interface is governed by the interface tension, which triggers the nucleation of a Ga-rich liquid phase at the triple junction to relieve the unbalanced interface tension increasing with Ga concentration. This finding underpins the importance of the interface (surface) tension governing the morphological evolution and structural stability of a nanoscale confined volume.

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Fig. 4. Magnified views of the triple junction configuration during the sublimation of Mg and corresponding schematic diagrams. Each phase is denoted by S (Solid Mg), V (Vapor) and L (Ga-rich liquid). (a) Stable configuration with a flat solid–vapor interface. The unbalanced interface tension $\gamma_{SV}$ is supported by the rigid cylinder. (b) Unstable configuration of the triple junction with a flat solid–vapor interface. The increased $\gamma_{SV}$ due to the Ga-enrichment causes the structural instability of solid Mg. (c) Stable configuration of the triple junction with the introduction of Ga-rich liquid phase. The liquid phase forms a ridge at the triple junction and its interface tensions with the solid Mg ($\gamma_{LS}$) and with the vapor ($\gamma_{LV}$) counterbalance the solid–vapor interface tension $\gamma_{SV}$ of Mg.

interface motion, but plays an important role in determining the shape of the interface. As the solid–vapor interface becomes enriched by Ga with the continued sublimation of Mg, the interface energy (tension) increases accordingly because the surface energy of Ga (0.881 J m\textsuperscript{-2} at 0 K) is larger than that of Mg (0.785 J m\textsuperscript{-2} at 0 K) [17] (as schematically delineated in Fig. 4(b)). When this unbalanced interface tension reaches a certain value, it causes (elastic) deformation of the solid Mg as manifested by repeated fluctuation in the TEM diffraction contrast (Fig. 2(b)–(d) and Supplementary Movie 3). This structural instability is relieved only when the interface develops a ridge with the formation of Ga-rich liquid phase. This behavior suggests that the increasing interface tension ($\gamma_{SV}$) with Ga concentration triggers the formation of the Ga-rich liquid phase. As this liquid phase forms a ridge, its $\gamma_{LS}$ and the $\gamma_{LV}$, counterbalance the $\gamma_{SV}$ (Fig. 4(c)).

In summary, the present study shows that the high energy Ga\textsuperscript{+} ion beam not only modifies the microstructure, but also affects the thermodynamic stability of a miniaturized metal prepared by FIB. The structural defects such as dislocation loops induced by high energy