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Nanomolding of crystalline metals: The smaller the easier

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We report a thermomechanical nanomolding method for crystalline metals. Based on atomic diffusion, this process becomes easier with decreasing mold diameter. As the responsible underlying diffusion mechanism is present in all metals and alloys, discovered nanomolding process provides a toolbox to shape essentially any metal and alloy into nanofeatures. Technologically, this highly versatile and practical thermomechanical nanomolding technique offers a method to fabricate high-surface area metallic nanostructures which are impactful in diverse fields of applications including catalysts, sensors, photovoltaics, microelectronics, and plasmonics.

Molding is a manufacturing process in which a pliable or moldable material is formed to replicate a mold. It is used as a processing technique for all major material classes, and the most versatile manufacturing technique for shaping of thermoplastics. The moldability of a material is typically associated with its flow-ability. Such flow-ability is high in thermoplastics, gels, and some glasses, however, low in crystalline metals [1,2]. Metals are either too hard in their crystalline state or too fluid and reactive in their liquid state to be considered for molding. The difficulty of a shape to be molded can be quantified in the aspect ratio between mold cavity depth, L , and mold cavity diameter, d . In general, molding is increasingly more challenging with decreasing d , which can originate from capillary forces [3] or intrinsic size effects, typically related with the length-scale of flow units [4]. Such flow units can be grains in crystalline metals (typically microns) or chain length in plastics (typically nanometers), or shear transformation

zones in metallic glasses (typically ~ 1 nanometers). Therefore, attempts to mold on the nanoscale have been limited to thermoplastics [2,5-8], gels [9-11], and glasses [12-15] due to their high mold-ability and small flow units. Crystalline metals have not been considered until recently, where we reported first evidence that, at high temperature of $\sim 0.6T_m$, some crystalline metals can be shaped into nanorods [16]. Here, we uncover the underlying mechanism for thermo-mechanical nanomolding with crystalline metals (TMNM with CM) as a diffusion dominated mechanism driven by the vacancy concentration gradient which follows the pressure gradient. Diffusion can either occur through a bulk or surface/interface process, and the ratio of the effectiveness of the two processes depends on the mold diameter and the mold/metal combinations. The scaling of the two processes ($L/d \propto 1/d$ for bulk and $L/d \propto 1/d^2$ for surface) suggests that molding becomes easier with decreasing mold size, and that essentially any metal can be molded into high aspect-ratio and single crystalline nanorods, as we show and explain, through TMNM with CM.

Introduced nanomolding with crystalline metals is a thermomechanical process (Fig. 1a), where a piece of crystalline metal is formed against a hard mold under a pressure (typically $p \geq 100$ MPa) and temperature (typically $T \geq 0.5 T_m$). By using this method, crystalline metals can be molded into millimeter, micrometer, and nanometer sized features (Fig. 1b). Surprisingly, for identical molding conditions, the ease of molding, quantified by the aspect ratio (L/d) of the molded rods increases rapidly with decreasing mold cavity (Fig. 1b-c, similar results are shown in Fig. S1 for TMNM with Fe) and suggesting that TMNM with CM becomes easier with decreasing mold cavity. This is opposite to other nanomolding methods such as thermoplastic molding of metallic glasses [3,4,17,18], laser shock imprinting [19], liquid printing [20], and dip-pen nanolithography [21], for which smaller and higher aspect-ratio features are typically increasing more challenging.

In general, the dominated deformation mechanism for crystalline metals can be either dislocation slip [22,23], twining [24,25], or grain boundary sliding or rotation [26,27], depending on the grain size [28]. In our experiments, very few twins are present in the prepared metallic nanorods, and the mold dimension is large compare to the grain size [16]. Therefore, we can rule

out twining or grain boundary sliding/rotation dominated deformation mechanisms. On the other hand, dislocation nucleation and movement will become increasingly less effective with decreasing mold size since the dislocation nucleation rate decreases sharply with decreasing mold diameter [29,30]. Hence, the observed “The smaller the easier” of TMNM with CM must originate from another mechanism. We suggest, and then quantify, that a mechanism based on diffusion is the underlying mechanism (Fig. 1d).

Typically during nanomolding of thermoplastics, gels, and glasses, decreasing of the mold cavity results in additional resistance to materials’ flow [3] [4]. This has been widely studied for nanomolding with bulk metallic glasses (BMGs) [3,18,31]. Results for an example system, $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ are shown as black solid squares in Fig. 2a [4]. The scaling of the moldability, L/d with mold diameter for this example is qualitatively different from TMNM with CM (Fig. 1c and red solid pentagons in Fig. 2a). Nanomolding of bulk metallic glasses is based on viscous flow, referred to as Hagen-Poiseuille flow [3,18]

$$\dot{u}_v \triangleq \frac{dL}{dt} = \frac{1}{64\eta\lambda} (4\gamma \cos \theta + pd) \propto d \quad (1)$$

where η is the viscosity, $\lambda = L/d$, γ is the surface energy of the supercooled liquid, and θ is the contact angle between the supercooled liquid metals and mold [3,32].

Integrating eq. (1) with respect to time enables to quantify $L/d(d)$. Results for nanomolding with BMGs and for TMNM with Au (see Supplementary Materials) are displayed in Fig. 2a. Obviously, nanomolding with BMGs is qualitatively different from TMNM with CM. Nanomolding with BMGs becomes more difficult with decreasing of mold diameter (or independent without capillary forces ($\theta = 90^\circ$) [4,33]). In sharp contrast, TMNM with CM becomes easier with decreasing mold size. These quantitative different behaviors suggest a mechanism for the TMNM with CM that scales with $1/d^n$ (with $n > 0$). Size comparisons rule out grain boundary sliding or rotation mechanisms [27]. The grain size of the used metals here is on the order of $10^1 \mu\text{m}$ [16], which is at least two orders of magnitude larger than the considered mold cavity diameters. Further, the scaling of $L/d(d)$ also excludes dislocation dominated deformation as the underlying dominant mechanism for TMNM with CM because dislocation nucleation rate and movement rapidly decrease with decreasing d due to the size effect in

plasticity [34,35]. A mechanism that scales as $1/d^n$ (with $n > 0$) is diffusion. Taking 1D random diffusion for example, the diffusion distance can be estimated by $L_D = \sqrt{D_b t}$. Substituting typical values for self-diffusivity of Au at 500°C, of $D_b = 15.7 \text{ nm}^2/\text{s}$ [36], for a typical experimental timescale of 100 s results in a random diffusion length of $L_D \approx 40 \text{ nm}$. Such estimation suggests smaller length scales than experimentally observed without an overall driving force for diffusion. However, as the pressure varies along the forming nanorod (see Fig. 3), so does the vacancy concentration. Hence diffusion into the mold cavity is not a random diffusion process but driven by a gradient of vacancy concentration. Considering that the diffusion path can either go through the lattice or the surface [37,38] (here instead of surface the mold/CM interface), we separately calculate the grows rates for lattice diffusion and interface diffusion by assuming that vacancy concentration only varies along the axis of the nanorod (1D model, see Supplementary Materials)

$$\dot{u}_L = \frac{p\Omega D_L}{kT\lambda} \left(1 - \frac{2\delta}{d}\right)^2 \frac{1}{d} \propto \frac{1}{d} \text{ for } \delta \ll d; \quad \dot{u}_I = \frac{4\dot{Q}_I}{\pi d^2} = \frac{4p\Omega\delta D_I}{kT\lambda} \left(1 - \frac{2\delta}{d}\right) \frac{1}{d^2} \propto \frac{1}{d^2} \text{ for } \delta \ll d \quad (2)$$

where $\Omega = 4\pi r_0^3 / 3$ is the atomic volume, r_0 the atomic radius, δ the interface thickness, D_L the lattice diffusion coefficient, and D_I the interface diffusion coefficient.

Eq. (2) reveals that both diffusion based mechanisms result in a grows rate inversely proportional to d . Such behavior is qualitatively consistent with our experimental observations (Fig. 1c, Fig. 2a and Fig. S1). To compare diffusion based growth (lattice and interface) of metallic nanorods with the viscous flow based nanomolding of BMGs, the grows rates for typical nanomolding of Pt-BMG and diffusion based growth of Au at 500°C are calculated (Fig. 2b). The diffusion controlled mechanism are qualitatively in agreement with our experimental data whereas the viscous flow behavior is not. When assuming that the interface diffusivity is ten times faster than the lattice diffusivity, below $d \sim 10 \text{ nm}$, interface controlled growth would be the more efficient mechanism. However, as the interface diffusivity is unknown and will be highly sensitive to mold/CM combinations, the cross-over of interface diffusion dominated grows at $\sim 10 \text{ nm}$ has a large uncertainty as it is only estimated and may vary significantly.

To quantitatively compare the diffusion based mechanism with the experimentally determined aspect-ratio of metallic nanorods, we add both diffusion processes as they can independently and simultaneously occur and integrate eq. (2) with respect to time, we get

$$\frac{L}{d} = \sqrt{\left(\frac{L_0}{d}\right)^2 + \frac{2p\Omega D_L t}{kTd^2} \left(1 + 4\frac{D_I \delta}{D_L d}\right)} \quad \text{for } \delta \ll d \quad (3)$$

L_0 is the depth of metal filling into the mold when the loading force reaches its maximum value. Equation (3) predicts $L/d \propto t^{1/2}$. To test this prediction, we experimentally varied the molding time while keeping all other processing conditions constant (see Supplementary Materials). We found a good description of eq. (3) to the experimental data (Fig. 2c). It is worth mentioning that $\frac{\partial^2(L/d)}{\partial t^2} < 0$, indicating a decreasing grows rate with increasing mold time. Such decreasing of grows rate originates from a decreasing gradient between the pressure at the tip of the nanorod and the pressure above the mold cavity, $\Delta p \approx p/L$. Most importantly, the predictions of eq. (3) agreeing well with the experimental data reveal that the mechanism of TMNM with CM is diffusion dominated. However, it must be noted that the lattice diffusion mechanism predicts a size-independent grows length while an interface diffusion mechanism results in a grows length inversely proportional to the mold size (eq. 3). If we plot the experimental data in Fig. 2a (red solid pentagons) as $L(d)$ (Fig. S2), we found that the grows length of Au nanorods is approximately constant, however with a superimposed term. Such term, which is proportional to the mold size, can be attributed to dislocation motion as slip system become increasingly activated with increasing mold size under the high forming pressure of ~ 800 MPa.

To further identify the mechanism for TMNM with CM and characterize the orientation of the growing nanorod, we used TEM (see Supplementary Materials) (Fig. 3a-d). We found for the considered Au nanorods that all are essentially single crystals growing along [110]. Often, close to the tip, few of twins are observed (Fig. 3c, HRTEM images at local regions i, ii and iii are shown in Fig. S3). The preferred orientation of the Au nanorods along [110] during experimental growth may originate from the anisotropy of self-diffusion in crystalline metals. As the {110} planes are the loosest packed planes, diffusion occurs most rapidly along [110] (see e.g. Refs.

[39]). At the entry of the mold cavity, some small crystals can be found (Fig. 3d, see also Fig. S4).

Based on the TEM investigations (Fig. 3a-d), growth scaling and velocity observations (Fig. 2), we propose the following atomic-scale mechanism for TMNM with CM (Fig. 3e-g): The pressure gradient from entry to tip along the cavity depth results in a vacancy concentration gradient. Diffusion occurs predominately along this gradient. As the feedstock from which the nanorods are molded comprises of crystals with random orientations, generally a change in orientation is required to form the observed [110] nanorods. This occurs at the entrance to the mold cavity where often several small crystals with “rotating” orientations towards [110] can be observed (Fig. 3d and Fig. S4). This suggests that the originally growth of nanorods follows the orientation of the feedstock crystal. As this orientation is generally not [110], a faster growing crystal with an orientation closer or of [110] may nucleate and eventually [110] oriented crystal forms and prevails to continue to grow into very high aspect-ratio nanorods. During growth, particularly close to the tip or at branches, twins can be readily formed to maintain the preferred [110] direction with little energy cost, which indicates that shear mechanism based twinning deformation can also contribute to the growth of Au nanorods. However, the observed very few twins in the prepared metallic nanorods (Fig. 3 or Ref. 16) indicate that the twinning is not the dominated deformation mechanism in TMNM with CM.

One of the major findings of our work is that molding becomes easier with decreasing mold size, quantified by a decreasing function L/d with d . This scaling naturally results from the scaling of the underlying diffusion controlled mechanism. For lattice diffusion, eq. (2) suggests $L/d \propto 1/d$ whereas for interface diffusion $L/d \propto 1/d^2$. Our data suggest, particularly for $d > 10$ nm, a predominant lattice diffusion dominated mechanism. However, this may be superimposed by an interface diffusion mechanism, particularly for $d < 10$ nm. The effectiveness of the interface diffusion mechanism strongly depends on the mold material and moldable crystalline metal and hence, can dominate the transport mechanism. In that case, the additional $1/d^2$ (to the $1/d$) originates from the increasing surface to volume ratio with decreasing d . Experimentally, fabricating smallest nanofeatures by TMNM with CM is limited by available molds. For the

smallest mold size of 5 nm considered in our experiments, we found that L/d follows the trend suggested by eq. (3) (Fig. 2a) and the aspect-ratios of the molded Au nanowires arrays are as high as ~ 340 (Fig. 2a).

Beside the capability of TMNM with CM to fabricate smallest-in-diameter nanorods, another demonstration of versatility requires study of the range of materials that can be formed by TMNM. Opposite to most practical nanofabrication techniques, TMNM should be possible with essentially all metals and alloys as the underlying diffusion mechanism is present in all metals and alloys. To demonstrate such a versatility, we considered various metals, including metals with different crystal structures, and a range of alloys to the extreme case of high entropy alloys. Specifically, we considered gold, nickel (f.c.c), vanadium (b.c.c), iron (b.c.c), $\text{Ag}_{75}\text{Ge}_{25}$, $\text{Ni}_{60}\text{Ti}_{40}$, $\text{Cu}_{34.7}\text{Zn}_{3.0}\text{Sn}_{62.3}$, PdCuNi and PdCuNiPtRhIr (Fig. 4a-i, see Supplementary Materials for the casting of alloys). For all considered metals and alloys, high aspect-ratio nanorods can be readily fabricated using TMNM with CM.

In summary, we revealed the underlying mechanism for thermomechanical nanomolding with crystalline metals as a diffusion controlled growth mechanism. Such mechanism results in single crystal molding of high aspect-ratio nanorods arrays and becomes easier with decreasing nanorod diameter. The presence of underlying diffusion mechanism in all metals and alloys suggests that TMNM with CM is applicable to essentially all metals and alloys. This is different from the vast majority of nanomolding methods that are typically limited to specific materials and/or by the size and aspect-ratio ranges. Such versatility and practicality of thermomechanical nanomolding with crystalline metals indicate a period of rapid progress and novel exploration of metal based nanomaterials.

Figure captions:

FIG. 1. Scaling of thermomechanical molding with crystalline metals. (a) Schematics of the experimental set-up of TMNM with CM. (b) Thermomechanical molding, taking Ag as an example, with millimeter, micrometer, and nanometer size molds, using molding pressure, temperature, and time of 100 MPa, 620°C, and 100 s, respectively. Examples of prepared Ag rods with diameters of 0.57 mm, 10 μm , 375 nm and 36 nm are shown in (i), (ii), (iii) and (iv). (c) Aspect ratio of the molded Ag rods as the function of mold diameter (d) (dashed-red line is given as guide to the eye). (d) The various dominant deformation mechanisms at play during thermomechanical molding at various length scales. Plastic deformation of metals is generally associated with dislocations from grain boundary sources and intragranular sources such as grain sliding and rotating. These processes become decreasingly and rapidly less effective with decreasing mold size. Hence, diffusion, becomes the dominant deformation mechanism on the nanoscale.

FIG. 2. Deformation mechanism of TMNM with CM compared to other nanomolding mechanisms. (a) Moldability, quantified by L/d , scales qualitatively different for bulk metallic glasses (black solid squares, the data are from Ref. [4]), and for crystalline metals (red solid pentagons, the dashed-red line is guide for the eye). The processing of Au nanorods was carried out at 622°C under ~ 800 MPa for 100 s. Hagen-Poiseuille law (H-P law) with capillary force where $\gamma = 1$ N/m and $\theta = 120^\circ$ [10] (magenta line) or without capillary force (blue line) are calculated. The molding time and loading pressure are 180 s and ~ 350 MPa, respectively, taking from Ref. [4]. The discrepancy between theory (magenta line) and experiments (black solid squares) is attributed to an enhanced viscosity on the nanoscale [4]. (b) Calculated grows rates for the diffusion driven growth of Au nanorods at 500°C (eq. 2, red and blue lines). Viscous flow based mechanism with and without capillary effect for nanomolding of Pt-BMG are also plotted for comparison (eq. 1, black and dashed-black lines). The loading pressure and aspect ratio are 500 MPa and $\lambda = 5$, respectively. The other parameters are taken from literatures and listed in Table S1. (c) Growth of Au nanorods at 500°C and ~ 500 MPa versus mold time. The dots represent the experimental data and the solid line calculated according to eq. (3).

FIG. 3. Atomic growth mechanism of thermomechanical nanomolding with crystalline metals. a-c. TEM images from a 50 nm Au nanorod fabricated by TMNM. (a) A bright field image of an Au nanorod. Its corresponding selected area electron diffraction pattern (inset) reveals the grows direction as [110]. Scale bar for inset is 0.4 $1/\text{\AA}$ (b-c) Zoom-in images of the tip region (b and c are captured from yellow and orange rectangles in a and b, respectively). Twins are revealed with twin planes of $\{111\}$ close to a tip and $\{111\}$ facets at the tip. $\{111\}$ planes are marked by red-dashed lines in (b) and (c). $\langle 112 \rangle$ directions are indicated as blue arrows in (c) to highlight mirror-like symmetrical characteristics on the twin boundaries. Twins can be generated to release local energy or misfit upon growing, which is commonly observed in face-centered cubic

Au. (d) A TEM image from a ~100 nm Au nanorod showing multiple grains with different crystallographic orientations at the root of the nanorod. (e-g) Schematics of TMNM with CM indicating atomistic processes as a sequence of grows of a metal nanorod and corresponding pressure profiles along its axis. Blue arrows represent $\langle 112 \rangle$ direction vectors. (e) A feedstock metal (here for f.c.c) is positioned on the mold at the molding temperature and a molding pressure is applied. (f) The applied pressure and temperature result in diffusion down the pressure gradient, which causes a vacancy gradient. As the initial orientation of the feedstock metal consist of multiple and randomly oriented grains, grows originally starts along a non-preferred orientation. This causes nucleation of new grains which progressively toward more preferred orientation (for f.c.c closer to $[110]$). There are two possible and size dependent diffusion mechanisms: i) interface diffusion along the mold/metal interface (Path 1) and ii) lattice diffusion through the rod (Path 2). (g) A rod at a later stage of molding which contains small crystals on the root, a long region of perfect single crystal which can exceed $L/d > 100$, and twins and faceted edges at the tip.

FIG. 4. Examples of fabricated nanorods arrays through TMNM with CM. (a) Au nanorods of 5-13 nm in diameter, formed under a pressure of ~500 MPa at 500°C for 100 s. (b) TMNM with Ni (f.c.c) at 600 MPa and at 600°C for 240 s. (c) TMNM with V (b.c.c) at 437 MPa and at 650°C for 100 s. (d) TMNM with Fe (b.c.c) at 400 MPa and at 600°C for 240 s. (e) TMNM with $\text{Ni}_{60}\text{Ti}_{40}$ at 650°C, under the forming pressure of 800 MPa for 180 s. (f-g) TMNM with $\text{Ag}_{75}\text{Ge}_{25}$ and $\text{Cu}_{34.7}\text{Zn}_{3.0}\text{Sn}_{62.3}$ at 500°C, loaded to ~ 350 MPa under a constant loading rate of 1.8 mm/min. (h) TMNM with PdCuNi at 695°C, under the forming pressure of 800 MPa for 180 s. (i) TMNM with high entropy alloy (PdCuNiPtRhIr) at 650°C, under the forming pressure of ~1000 MPa for 180 s.

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