100 interstitials diffuse with a low activation energy and a pre-exponential factor that decreases with increasing loop size. Similar diffusion behavior occurs in FCC metals like copper, although loop diffusivity decreases for loops containing more than about 50 interstitials because the perfect dislocation separates into partial dislocations bounding a stacking fault. Few simulations of perfect vacancy loops have been performed, because they are not believed as mobile as interstitial loops.

Molecular dynamics simulations of interstitial loops containing more than a few hundred interstitials have not been performed. This is because loop migration is expected to decrease to zero as the loop size approaches the size at which thermal diffusivity ceases. In the larger size limit, it is well known that the motion of dislocations in response to an applied stress controls the mechanical behavior of metals. In fact, the serrated or saw-toothed stress-strain response of BCC metals in tension tests is explained by the interaction of dislocations with nearby impurity atoms like carbon and nitrogen. The impurity atoms surrounding a dislocation are termed a “Cottrell atmosphere” (8), and the repeated motion of the dislocation away from the atmosphere, followed by diffusion of the impurities to the dislocation, explains the observed stress-strain behavior.

On page 956 of this issue, Arakawa et al. (2) show that interstitial-type dislocation loops with sizes between 6 and 20 nm undergo thermally induced one-dimensional diffusion in BCC iron with a constant 1.3 eV activation barrier, independent of loop size. The authors propose that the loop diffusivity is controlled by the interaction with interstitial impurity atoms akin to the Cottrell atmospheres.

In some sense, these results agree with current knowledge, namely one-dimensional diffusion of dislocation loops controlled by the collective motion of dislocations and impurity atoms. However, these loops are larger than observed in MD simulations and yet quite small compared with conventional dislocations. Additionally, the activation energies and pre-exponential factors of loop diffusivity are larger than in MD simulations, and it is unclear whether the thermal diffusion of dislocation loops and impurities occurs by the same mechanism as the stress-driven coupled diffusion of a Cottrell atmosphere.

On page 959 of this issue, Matsukawa and Zinkle (3) demonstrate that prismatic vacancy-type dislocation loops with sizes between 2 and 3.4 nm undergo thermally induced one-dimensional diffusion in gold. The authors did not quantify the loop diffusivity, but estimate an activation energy of ~0.22 eV. The observation confirms the perception of low diffusivity and requires new knowledge to determine the diffusion mechanism. Additionally, and perhaps more surprising, the authors observe direct transformation of a perfect, prismatic loop into a stacking fault tetrahedron. Such a transformation, and the mechanism by which it occurs, have received limited study.

Taken together, these results expand the knowledge of dislocation loop behavior, and raise new questions about the size dependence of loop diffusion, the mechanisms controlling loop and impurity interactions, as well as possible transformation mechanisms between defect cluster configurations. This will motivate additional theoretical, computational, and experimental investigations. Yet, in this age of nanomaterials, where manipulation of the arrangement and ordering of materials across nanometer length scales is becoming routine, the articles should also stimulate innovative strategies to pattern, or self-organize, defects and solute structures as a result of one-dimensional diffusion, leading to tunable material properties.

References

CHEMISTRY

Enhancing Colloids Through the Surface

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Colloidal particles are used in many consumer and industrial products, from cosmetics and pharmaceuticals to adhesives and paints. In these applications, the colloidal particles are usually spherical and have homogeneous surfaces. If their assembly could be influenced by manipulating the surface chemistry of the particles, new opportunities for colloidal materials could emerge. For example, proposed phononic applications—as chemical sensors, optical filters, or interconnects—could be realized if colloidal crystals could be assembled into new symmetries with large, defect-tolerant phononic band gaps. Surface-modified colloids and colloidal crystals may also be used in biological, microelectronic, and catalytic applications.

In a traditional colloidal system, the colloidal surface is coated with charged moieties, which stabilize the colloids in solution. Upon drying, a close-packed colloidal crystal up to hundreds of layers thick with varying defect densities may form. Most colloidal systems pack into a face-centered cubic structure, but oppositely charged colloids can form ionic crystals (1). To create even more complex structures, the colloidal particles must exhibit directional interactions. This can potentially be achieved by chemically modifying specific regions of the colloidal surface.

Systems with chemical anisotropy have great promise for forming new structures with otherwise unattainable properties (2). Theoretical studies by Zhang et al. indicate that colloids with four attractive patches on the colloidal surface that form the corners of a tetrahedron can self-assemble from a disordered state into a crystal with diamond symmetry (see the first figure) (3). This structure is of great interest for phononic applications because of the large phononic band gap it has been proposed to possess. This structure has yet to be realized through self-assembly, but recent experimental advances in synthesizing and assembling colloids with chemically distinct patches may soon make this goal achievable.

For example, it is now possible to synthe-
size “Janus” particles with chemically distinct hemispheres. However, synthesis is only the first step toward enhancing the function of colloidal systems. Assembly must also be controlled, posing potentially more difficult problems. Such Janus colloidal particles have been shown to form minimum-energy clusters of 2 to 12 colloids (4), but these clusters have not yet been shown to assemble into a macroscopic crystal. Colloids with more complex patches have been patterned using multilayer colloidal crystals as a physical mask; however, the yields are low, and it is not obvious how the process can be scaled up to sufficient volumes of particles to study assembly (5). In another approach, microspheres of like charge were bound together with nanoparticles of opposite charge to form clusters of two to nine colloids. The loading of nanoparticles was varied to adjust the cluster surface from mostly bare to predominantly nanoparticle-covered (6); assembly of these particles has yet to be explored.

But it remains highly challenging to assemble more complex objects or to form assemblies with long-range order. There have been successes in directed assembly of colloids into large-scale structures. For example, Dinsmore et al. (7) created complex structures by assembling colloidal crystal shells at interfaces in a water-oil emulsion. These “colloidosomes” have controlled pore sizes that can be used to selectively allow permeation of the shell by various molecular species. In another study, Hermanson et al. used dielectrophoresis to assemble metallic colloids into self-repairing conductive wires with millimeter-scale order (8). These approaches to assembling large-scale structures are promising, but do not yield structures with local order. Ligand-directed assembly may potentially provide the specificity necessary to impart both the desired local and long-range structure.

DNA is an ideal ligand for directing assembly because of its high specificity, reversibility, and unique ability to assemble structures over both the nanometer and the micrometer scale. DNA hybridization has, for example, been used to assemble gold nanoparticles (9) and micrometer-scale polystyrene colloids (10). Biancianello and co-workers have even formed small colloidal crystals through DNA-directed assembly of polystyrene microspheres (11). These initial demonstrations were rather simple, but it should be possible to form much more complex structures through DNA-directed assembly. The reversibility of DNA hybridization may even allow selective defect removal.

Although colloids with homogeneous coatings of molecules having binding specificity, such as DNA, have been synthesized, it was not until recently that individual reactive molecules were patterned on precise locations of the colloidal surface. By placing individual reactive molecules at the poles of gold particles, DeVries et al. formed monomers that could be polymerized into linear nanoparticle chains (12). The authors first coated the colloid with a self-assembled monolayer and then exchanged the molecules at the poles of the colloid with reactive, functional molecules. This exchange occurs specifically at the poles of the spherical particle, where the self-assembled monolayer is unstable and easy to exchange. Similar nanoparticle chains have shown great potential for optical devices, such as waveguides (13).

In an interesting new approach for using surface chemistry to enhance the function of colloids, Plunkett and co-workers have synthesized colloids with reversibly photoswitchable surface charge. Upon irradiation, these colloids convert from an aggregated, oppositely charged structure to a dispersed, like-charged structure, a first step toward photoresponsive colloidal crystallization (see the second figure) (14). Such photoswitchable systems are a general route to driving colloidal synthesis of site-specific patterned colloids. Exact control of patch size and location is difficult. General patch functionalization schemes need to be developed. Reversible interactions will also be necessary to remove defects. Here, photoswitchable systems show promise. As functionalization strategies mature, investigations into the assembly of chemically modified colloids should provide important feedback to determine the requirements for specificity, binding strength, range of interactions, and reversibility necessary to achieve the desired interactions and assembly through chemical modification of the colloidal surface. Success should yield new materials for photonic and electronic applications, consumer products, and industrial systems due to the unique properties enabled by surface-modified colloids.

References