METALLIC GLASSES

Family traits

The finding that metallic glasses inherit their elastic properties from solvent atoms leads to a new understanding of the complex relationship between glassy structure, deformation and mechanical properties.

Wei Hua Wang

The disordered atomic structure of metallic glasses gives rise to unique mechanical and physical properties such as strength and elasticity, and are being considered for a wide range of applications. However, to understand and ultimately control these properties, it is important to study their disordered structure. Seen on the macroscale, metallic glasses are isotropic and homogeneous. On the microscopic scale, however, it is clear the situation is far more complex. There is a short-range order on the atomic scale with clusters of solute atoms surrounded by a majority of solvent atoms. There is also a nanoscale medium-range order that can be modelled by highly structured superclusters consisting of interconnected smaller clusters[1,2]. Both short- and medium-range orders affect the properties of metallic glasses, but they are extremely difficult to distinguish. The way the atoms pack inside metallic glasses and the role the local atomic order plays in their deformation remains a mystery; our understanding of the glassy structure so far relies to a large extent on models and simulations. In one of the few experimental studies on this topic, Dong Ma and colleagues now show how the metallic glasses inherit the elastic moduli from their solvent components[3].

Elastic modulus describes the reversible shape change of solids under an applied stress. For example, the shear modulus is related to the strain response of a solid under shear stress and represents its shear strain resistance. The most commonly used elastic modulus in engineering is Young's modulus, named after the nineteenth-century British scientist Thomas Young, and is defined as the ratio of uniaxial stress to strain in the solid's elastic regime. Microscopically, both types of moduli reflect the inherent stiffness of atomic bonds[4–6]. To explore the structural origin of the moduli in metallic glasses, Ma and colleagues carried out an *in situ* neutron diffraction study on an elastically deformed metallic glass to determine the response of the local atomic structures to stress. By comparing the Young and shear moduli of various metallic glasses with their base elements (that is, their solvent components), they found that the moduli of the glasses were almost equal to their solvents (Fig. 1a). This indicates that the elastic moduli of the metallic glasses are primarily determined by their solvent metals and that it is the solvents that are responsible for the overall stiffness and rigidity. This is surprising, because the base element normally makes up only about half of such glasses.

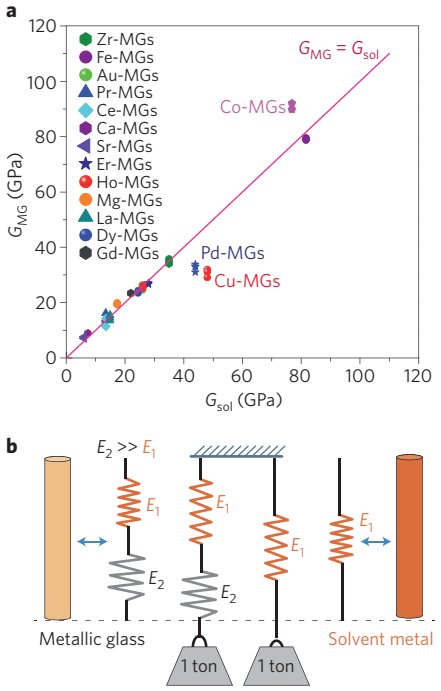

Figure 1 | Comparison between elastic moduli of metallic glasses and their solvent metals. **a**, The average ratio of shear modulus for various metallic glasses (G_{MG}) and their solvents (G_{sol}) is close to 1, indicating that moduli of metallic glasses are primarily determined by their solvent metals. The Cu-, Co- and Pd-based glasses markedly deviate from G_{sol}. **b**, Metallic glasses can be simply modelled as a stiff spring (representing the solute–solvent bonded cluster, modulus E_2) that connects in series with a much less stiff spring (representing the weak solvent–solvent bonding, modulus E_1) and therefore to the solvent metal itself. Under the application of a force the less stiff spring accommodates strain. The elastic moduli of the glasses are therefore inherited from the solvent metal.

Furthermore, careful data analysis enables the decomposition of the data into a strain-sensitive part that is related to medium-range order (the superclusters), and a strain-insensitive part related to short-range order (the solute-centred clusters). They further demonstrate that elastic deformation in metallic glasses mainly occurs at the solvent–solvent junctions among solute-centred clusters and/or superclusters, and that the moduli are essentially determined by the weakest solvent–solvent bonding. This implies that metallic glasses have a rubber-like structure, which can be viewed as consisting of stiff solute-centred clusters (similar to the molecular units in rubber) and much weaker solvent–solvent bonds linking the clusters, as shown in Fig. 1b. The experimental results support the so-called random-cluster-packing model for metallic glasses, and furthermore reveal the hierarchical atomic bands and inhomogeneous microstructure of metallic glasses.

However, although this represents an important step towards revealing the structural secret of metallic glasses, caution needs to be taken. For some systems such as Pd-, Cu- and Co-based metallic glasses, their moduli are markedly different from their base elements (Fig. 1a). Nevertheless, such deviations could help to understand different glass structural features. For example, the moduli of $Cu_{60}Zr_{20}Hf_{10}Ti_{10}$ glass are not close to those of its base element Cu, but is close to those of Zr, indicating that Zr and not Cu is its solvent[6].

The findings also provide valuable insight into the structural origin of the superior elasticity of metallic glasses. The conventional theory on the elasticity in glasses is that it occurs uniformly by straining the material on all length scales. However, as Ma and colleagues now show, not every component in a metallic glass contributes equally to the overall modulus (Fig. 1b). Only the least stiff spring (the weakest solvent–solvent bonds) accommodates the strain, and the elastic deformation is inhomogeneous.

The elastic moduli also have strong relations with the broader mechanical

properties of metallic glasses[4–6]. For this reason we anticipate a similar inheritance of properties from solvent components for these as well. Indeed, we already know that yield strength and plasticity of metallic glasses are to a large extent determined by solvent metals[6]: Zr-, Pt-, Pd-based glasses have a large compressive plasticity and toughness that is inherited from their solvent components[7,8]. Plasticity is known to be favoured by a high Poisson ratio[7] — a factor that can be used in choosing appropriate solvents for the synthesis of metallic glasses with large plasticity. The elastic modulus is therefore a good parameter for the design of new glasses.

The work of Ma and colleagues is also helpful for understanding not only the atomic bonding structures, the elasticity and mechanical properties of metallic glasses, but also the structural origin of irreversible plastic deformation and the glass transition. Theories have proposed that structural heterogeneities such as defects act as flow units that accommodate plastic deformation or initiate glass transition in glasses[9,10]. The activation of these flow units, which is uniquely related to shear modulus[4–6], should be closely related to the atomic bonds between solvents. The experiments by Ma and colleagues will certainly promote further studies that will explore the long-standing issue of plastic deformation and glass transition, and the relationship of these properties to elastic modulus. ❐

Wei Hua Wang is in the Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.
e-mail: whw@iphy.ac.cn

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DNA ORIGAMI

Nanorobots grab cellular control

Self-assembled barrel-like DNA nanostructures carrying active payloads and pre-programmed with logic operations to reconfigure in response to cell-surface cues can trigger a variety of intracellular functions.

Johann Elbaz and Itamar Willner

Rapid progress in DNA nanotechnology[1,2], particularly in the development of nucleic-acid-based machines[3,4], provides unparalleled opportunities to implement nanoscale nucleic acids as tools to control intra- or intercellular functions. This is now highlighted in a study reported in *Science* by George Church and co-workers, who demonstrate the programming and assembly of DNA-based nanorobots able to carry molecular loads, transport chemical ingredients to cells, and activate intracellular transformations[5]. The work builds on recent developments in DNA nanotechnology, including the self-assembly of DNA-origami nanostructures[6–8], the selective molecular-binding properties of sequence-specific nucleic acids[9] (also known as aptamers), the activation of DNA machines by external triggers[10], and the use of the information encoded in nucleic acids for logic operations and computing circuitries[11–13].

The nanorobot demonstrated by Church and co-authors consists of two clasps made of DNA origami that include protruding nucleic-acid chains for anchoring the molecular payload (Fig. 1). The clasps are held together by DNA duplexes to form a clam-shaped nanostructure, which provides a reservoir for the payload, and the DNA duplexes comprise aptamer sequences that act as 'locks' for the clam-shaped container. In the presence of appropriate cell-generated biomarkers — the 'keys', which act as substrates for the aptamer sequences — the formation of aptamer–substrate complexes unlocks the origami-based container, and this leads to the stimulation of intracellular functions through the exposure of the payload to the cell. Church and co-authors also implemented an AND logic operation that causes the robot to unlock only in the presence of two different biomarker 'keys' (Fig. 2).

The authors also showed how the robots can be used to stimulate cell signalling in specific cell types. For this, the payload carried by the nanorobots included antigen-binding antibody fragments incorporating the instructive information to bind and activate specific cells, and cell biomarkers from the targeted cells acted as inputs that triggered and unlocked the robots. In particular, clam-shaped robots locked by pairwise combinations of specific aptamer sequences targeting lymphocytic

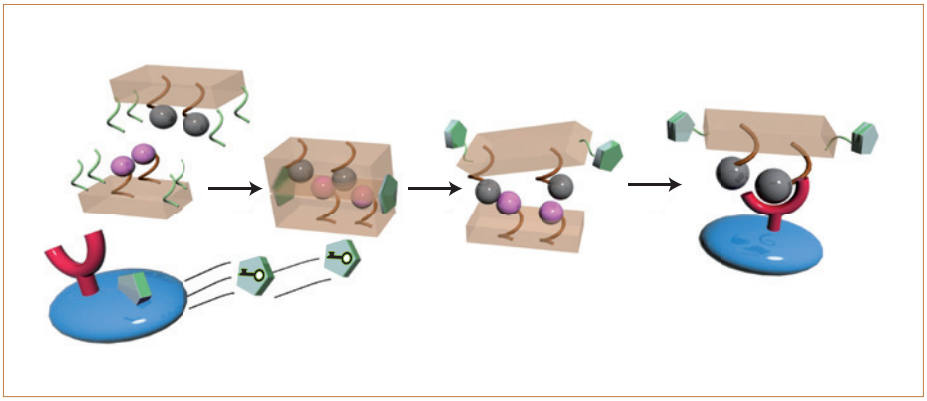

Figure 1 | Schematic of a clam-shaped nanorobot made of DNA origami (brown blocks) carrying active payloads (balls). The nanorobot spontaneously fastens through two complementary DNA-aptamer locks (green strands), opens up in the presence of a cell-produced biomarker (pentagons), and binds to the cell surface (blue disk) through specific host–guest interactions[5].