Materials science

Boundaries transformed in pure metals

Eugen Rabkin

Interfaces between the tiny crystal grains that make up solid copper have been shown to change from one ordered phase to another, independently of the phase adopted by the crystals, opening up prospects for materials development. **See p.375**

Some solid metals exist in various structural forms, a phenomenon known as polymorphism. Iron, for example, adopts one type of cubic lattice (α-iron) at room temperature, but transforms into another (γ-iron) above 912 °C. This is an example of a phase transformation — an abrupt change in the atomic structure of a material that occurs during a gradual change in temperature or pressure. The transformation of γ- to α-iron that occurs when iron alloyed with carbon is rapidly cooled from a high temperature has long been used to produce hard and strong steels; by contrast, pure iron is soft and ductile. On page 375, Meiners et al.[1] report that polymorphic phase transformations can also occur at the interfaces between the tiny crystals that make up most pure metals. This discovery suggests a fresh approach for processing metallic materials to optimize their properties for applications.

The vast majority of solid metals and their alloys are polycrystals — assemblies of billions of minuscule single crystals called grains, which are separated by grain boundaries. These boundaries are often the 'weak links' that cause a material to be brittle and to fracture.

> **"The images reveal the coexistence of two distinct atomic structures, which the authors refer to as domino and pearl phases."**

However, they can also be used to strengthen materials, because some grain boundaries efficiently block dislocation glide (a fundamental mechanism of plasticity in metals that involves the movement of lattice defects).

About a century ago, it was thought[2] that grain boundaries were amorphous layers about one micrometre thick. However, modern microscopy tools have revealed[3] that the distorted atomic structure in these boundaries is only a few ångströms thick, comparable to interatomic distances. It is also now known that the atomic structures of most grain boundaries can be thought of as periodic arrangements of certain atomic structural units[4] — that is, the grain boundaries can be thought of as two-dimensional crystals that have their own atomic structure, which is very different from the structure of the grains that they separate.

A key question is whether these 2D structures undergo phase transformations that are unrelated to those in adjoining grains. For alloys that consist of two or more components, the answer is a resounding 'yes'. Such phase transformations have been extensively characterized in experiments, and have been described by theoretical and computational models[5,6].

The situation was less clear for pure metals: indirect evidence[7,8] hinted that phase transformations are possible at grain boundaries in pure tin and copper, but no direct observations had been made. Observing changes in the atomic structure of a grain boundary is a daunting task, because only minor displacements of atoms at the boundary are required to change its structure, and the atoms move much faster in the boundary than in a grain[9].

Meiners et al. now report that grain-boundary phase transformations occur in pure copper. The authors studied several grain boundaries in thin copper films that had been deposited on sapphire substrates, under ultra-clean conditions to exclude any potential effects of impurities. Using a scanning transmission electron microscope, they directly imaged the positions of columns of atoms in the thin-film samples. Their atomic-resolution images reveal the coexistence of two distinct atomic structures in two grain boundaries that had similar geometric parameters, as would be expected during phase transformations. The authors refer to these structures as domino and pearl phases, on the basis of the patterns formed by the atoms within them (Fig. 1).

However, this observation alone does not constitute proof of a phase transformation, because one of the two phases could be in a highly unstable state that formed during the deposition of copper film, and that was preserved in the solid film on cooling. The authors therefore obtained further proof using a machine-learning approach (an evolutionary algorithm) in atomic computer simulations of a grain boundary that had the same geometry as the experimentally observed boundaries. The simulations showed that the pearl phase corresponds to the lowest-energy state of the grain boundary, whereas the domino phase
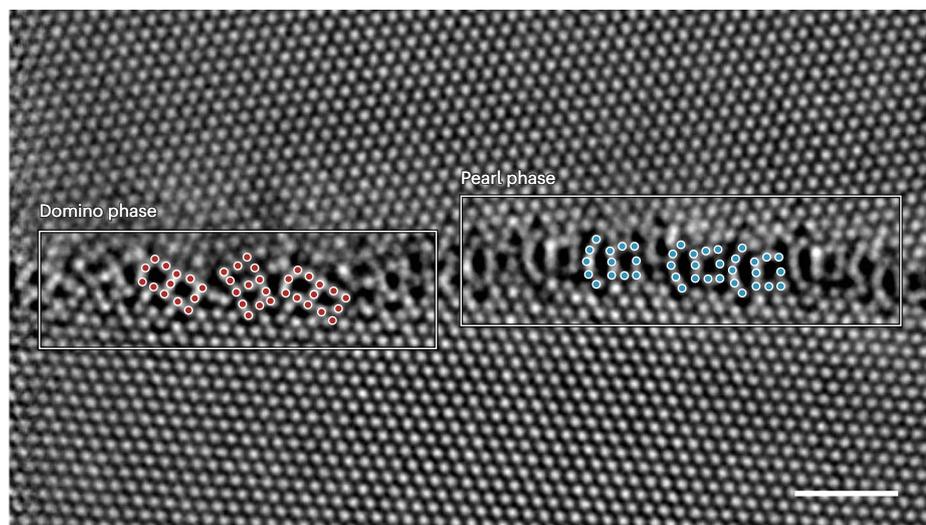

Figure 1 | Dominos and pearls. Most metals are assemblies of billions of tiny single crystals, called grains, which are separated by grain boundaries — layers of atoms that have a different periodic arrangement from that of the grains themselves. Meiners et al.[1] used high-resolution microscopy techniques to investigate grain boundaries in thin copper films deposited on sapphire, and observed two coexisting phases (pictured), which they named domino and pearl phases. The authors also observed these phases in atomic computer simulations (not shown) of a grain boundary that had the same geometry as the ones in the films. They conclude that phase transformations occur in the grain boundaries of copper, and therefore probably also in those of other pure metals. Scale bar, 1 nanometre. (Image taken from Fig. 1 of ref. 1.)

is in a metastable state. The simulations also showed that the metastable domino phase is stabilized when stress is applied perpendicularly to the plane of the simulated grain boundary, so that its energy matches that of the stable pearl phase — thereby establishing a true thermodynamic equilibrium between the two phases.

Meiners and colleagues' work clearly proves that phase transformations occur in the grain boundaries of pure metals, and thus opens up fresh opportunities for materials design. The number of possible polymorphs of bulk metals is generally limited, but the variety of grain-boundary structures and their possible metastable polymorphs (sometimes referred to as complexions[6]) is essentially boundless[10,11]. One can therefore envisage a processing technique that optimizes the overall performance of a material by producing grain-boundary phases (either stable or metastable) that maximize the positive effects of boundaries, but minimize their negative effects. For example, if one could produce grain-boundary polymorphs in aluminium that efficiently block dislocation glide (to maximize mechanical strength) and minimize electron scattering (minimizing electrical resistivity), the resulting metal would be a 'dream material' for making wire conductors in overhead power lines — eliminating the need for more-expensive aluminium-based composite wires.

However, it remains to be seen whether the full potential of engineering phase transformations at grain boundaries can be realized in practice. One reason is that it is not clear how processing methods could be designed that produce desired grain-boundary phases. Moreover, a similar concept known as grain-boundary engineering[12] — the use of processing methods to obtain grain boundaries that have a desired geometry and properties, without using phase transformations — has so far yielded only modest practical results.

Another issue is that the large number of possible grain-boundary polymorphs will make it difficult to systematically determine polymorph properties. High-throughput computational methods based on machine learning and big data will be of help here[1,13]. Indeed, Meiners and colleagues' work is a promising example of how the synergistic combination of high-resolution microscopy techniques and computational methods can lead to conceptual breakthroughs in the study of grain boundaries.

Eugen Rabkin is in the Department of Materials Science and Engineering, Technion – Israel Institute of Technology, 3200003 Haifa, Israel.
e-mail: erabkin@technion.ac.il

1. Meiners, T., Frolov, T., Rudd, R. E. & Dehm, G. & Liebscher, C. H. *Nature* **579**, 375–378 (2020).
2. Rosenhain, W. & Ewen, D. *J. Inst. Metals* **10**, 119–148 (1913).
3. Brandon, D. G. & Wald, M. *Phil. Mag.* **6**, 1035–1044 (1961).
4. Sutton, A. P. & Balluffi, R. W. *Interfaces in Crystalline Materials* (Oxford Univ. Press, 1995).
5. Rabkin, E. I., Semenov, V. N., Shvindlerman, L. S. & Straumal, B. B. *Acta Metall. Mater.* **39**, 627–639 (1991).
6. Cantwell, P. R. *et al. Acta Mater.* **62**, 1–48 (2014).
7. Maksimova, E. L., Shvindlerman, L. S. & Straumal, B. B. *Acta Metall.* **36**, 1573–1583 (1988).
8. Frolov, T., Divinski, S. V., Asta, M. & Mishin, Y. *Phys. Rev. Lett.* **110**, 255502 (2013).
9. Kaur, I., Mishin, Y. & Gust, W. *Fundamentals of Grain and Interphase Boundary Diffusion* 3rd edn (Wiley, 1995).
10. Rittner, J. D. & Seidman, D. N. *Phys. Rev. B* **54**, 6999–7015 (1996).
11. Han, J., Vitek, V. & Srolovitz, D. J. *Acta Mater.* **104**, 259–273 (2016).
12. Watanabe, T. & Tsurekawa, S. *Acta Mater.* **47**, 4171–4185 (1999).
13. Homer, E. R. *Comp. Mater. Sci.* **161**, 244–254 (2019).

Palaeontology

Poultry through time

Kevin Padian

A newly discovered 66.7-million-year-old fossil bird excavated in Belgium provides us with the best evidence so far for understanding when the living groups of birds first evolved and began to diverge. **See p.397**

The living groups of birds are amazingly diverse, numbering some 10,000 species, and endlessly fascinating. But when did they first evolve? The answer depends on how you define a bird, how you recognize the most basal (earliest diverging) birds in the fossil record, and how you account for the palaeontological and genetic gaps in our knowledge of bird evolution. On page 397, Field *et al*.[1] report the discovery of a fossil bird from 66.7 million years (Myr) ago, during the Late Cretaceous period, the most recent point in time currently known when the first representatives of today's birds evolved. In the process, the authors offer what might be a useful corrective to genetics-based estimates of the timing of bird diversification.

Most narratives of bird evolution begin with the pioneer *Archaeopteryx*, which first took wing in the Late Jurassic period (some 150 Myr ago) in present-day Germany[2]. *Archaeopteryx* is a bird in the broad sense of the term — it had a full complement of feathers and flew by flapping its wings — but it's far from having the hallmarks needed to group it with members of any living birds. *Archaeopteryx* has features that are so unspecialized that they don't prevent it from being the ancestor of all later bird groups, but they don't tell us whether living birds arose from this exact lineage.

When considering the relationships between any large group of organisms, such as birds, a key split on the evolutionary tree (Fig. 1) is the distinction between what are called crown-group and stem-group members[3]. For birds, the crown group includes all living birds (from ostriches to warblers, including quail, gulls, finches, woodpeckers, crows and all their relations), plus all descendants of their most recent common ancestor (that is, all the ancient ostriches, warblers and relatives of the other living bird groups). By contrast, the stem-group birds are those placed outside the living groups of birds but nevertheless still closer to them than they are to other major related groups, such as extinct dinosaurs: in other words, birds from *Archaeopteryx* (the most basal known bird) up to, but not including, living bird groups. The question is whether Field *et al*. are reporting on another stem-group bird or the first well-established crown-group bird, and what the age of their fossil discovery tells us about the timing of avian evolution.

All available evidence indicates that birds evolved from a group of carnivorous dinosaurs called theropods during the Jurassic period (about 200–145 Myr ago), and that bird flight had evolved by then, at least considering *Archaeopteryx*[2]. Through the Cretaceous period (145–66.5 Myr ago) there was considerable evolutionary experimentation in the early offshoots of bird lineages (in such diverse groups as the Enantiornithes, Hesperornithes and Ichthyornithes)[4]. But these ancient birds are outside the crown group because they lack the structural and physiological features characteristic of living birds. These stem-group birds seem to have grown much like small dinosaurs had done ever since the Triassic period (about 250–200 Myr ago) — faster than typical reptiles but slower than today's birds, reaching maturity in a few years, on the basis of examination of their bone tissues[5].

However, sometime during the latest Cretaceous, a stem-group lineage of birds evolved that had much higher growth rates than these more basal lineages, and that generally matured within a year or even sooner[2,5]. These became the crown-group birds. Their relationship to the closely related stem-group birds remains fuzzy, partly because fossil birds are