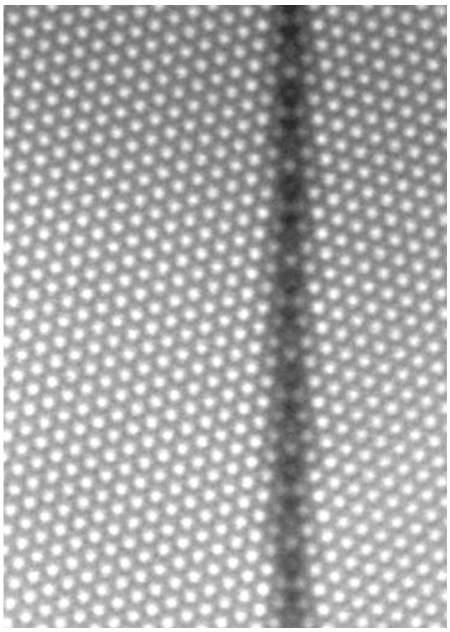
Phases at the interface

The area confined between grains in polycrystalline materials can undergo phase transformations under external stimuli, providing prospects for materials design based on grain boundary phase engineering.

The majority of crystalline materials are composed of many small single-crystal grains oriented in different directions, with the connection between grains called a grain boundary (GB). The grains do not simply join together with a sharp two-dimensional interface, but often consist of an interfacial transition region with a structure distinct from that of the adjacent grains, to accommodate their mismatch. GBs are normally considered as defects, with less ordered atomic arrangements compared to the region within the grains. These GB structures play an essential role in determining materials properties. GBs impede and interact with dislocations, providing an important strengthening mechanism in engineering materials. Impurity segregation or precipitation at grain boundaries is correlated with various intergranular degradation mechanisms such as embrittlement, cracking and corrosion. The presence of GBs also promotes certain catalytic reactions. Additionally, carrier transport across or through the GBs is strongly affected by the boundary structure and chemical composition, influencing thermal, electrical and other physical properties.

Interestingly, the structures of GBs may also change discontinuously, hence affecting properties, similarly to phase transformations occurring within the grains. It is noted that this type of transformation is sometimes referred to as a 'complexion' transition describing the variation of the thermodynamically stable states of an interface[1], while the use of this terminology is open to dispute[2]. The concept of GB phase transformation was first introduced more than 50 years ago[3]. Different interfacial structures and phases have been identified experimentally in various types of materials, yet the phase transition process has mostly been investigated by theoretical and computational efforts due to the challenges of tracking such fast and subtle individual atomic movements in experiments. Recently, some evidence of phase transformation was provided by the observation of two coexisting distinct phases at the same grain boundary in pure copper thin films at room temperature, with the transformation kinetics and phase stability further explored with simulations[4].

In an Article published in this issue of *Nature Materials*, Yuichi Ikuhara and colleagues reveal experimentally the atomic process of GB phase transformation in α-Al_2O_3, which is shown to facilitate GB migration. Using scanning transmission electron microscopy (STEM), they exploited electron beam irradiation close to a GB to trigger and control its motion within only a few atomic columns, and then captured its atomic structure with STEM imaging. By repeating this process, they recorded the structural evolution during the GB migration, showing that the GB transforms through different stable and metastable phases via collective atomic shuffling during migration. These results not only directly evidence the GB phase transformation, but also provide insights into GB migration, which is the dominating process governing crystal growth and bulk phase transformation, as suggested in an accompanying News & Views by Yuri Mishin. As discussed, however, many questions remain open-ended. For example, what would happen at higher temperatures activating other atomic motion mechanisms or with other defects involved in more complex scenarios? Moreover, how GBs migrate and transform more generally for other types of materials as well as under different conditions remains unclear.



A grain boundary structure. Credit: Jiake Wei, wei@sigma.t.u-tokyo.ac.jp

Among the open questions is the nature of the driving force for the GB phase transformation. Temperature and composition variations (for example due to chemical segregation) are natural drivers for interfacial phase transitions, as for bulk ones. Strain is another obvious candidate. In their work, Ikuhara and colleagues propose that point defects and the strain field generated by electron beam irradiation can contribute to the driving force, even if quantitative determination can be challenging. The role of other external stimuli such as electric or magnetic fields, the induced GB phase transformation pathways, as well as the ways to influence materials properties, remain largely elusive, and recent studies are looking experimentally into these issues[5].

The area between grains can be more confined in space and still hold distinct atomic arrangements. For instance, at triple junctions where more than two grains meet, a ceramic phase with translational periodicity in only one direction has been found, which presents a wide-bandgap semiconductor behaviour different from the bulk insulating phase[6]. One-dimensional (1D) ordered structures, extending across different structural units, have also been found at GBs in two-dimensional materials[7]. The potential phase transformations of these 1D interfacial structures are still waiting to be explored.

There is plenty of room at interfaces. While this area of research has significantly progressed in recent years, many fundamental questions remain regarding GB phase transformations, mainly due to the challenges of their experimental identification and quantification. Along with the mechanistic understanding and development of GB phase diagrams, the manipulation and utilization of GB phase transformations — GB phase engineering — are definitely worth exploring further. ❐

Published online: 29 June 2021
https://doi.org/10.1038/s41563-021-01049-5

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