of *Vps34* worsens the disease phenotype (*4*). This may relate to the multiple roles of Vps34, particularly its involvement in the initiation of autophagy, given that zebrafish and mouse models of XLMTM are sensitive to dysregulation of autophagy (*10*, *11*). Because menadione sodium bisulfite does not inhibit autophagy, it could be effective without deleterious effects. However, additional preclinical work is needed to assess the benefit of Vps34 inhibition, either alone or in combination with other small-molecule therapies that have shown efficacy in the XLMTM mouse model (*12*). There is also the emerging challenge of the underlying liver disease in XLMTM. It is intriguing to consider whether menadione sodium bisulfite may improve—or, instead, potentially worsen—XLMTM liver disease.

Vps34 is the primary generator of PI(3)P, a low-abundance membrane-bound phospholipid that serves as a signaling molecule to regulate membrane trafficking. Vps34 attracts proteins with PI(3)P-binding motifs, which in turn are involved with dynamic membrane remodeling and initiation of vesicle transport. The identification of menadione sodium bisulfite as an inhibitor of Vps34 by Swamynathan *et al.* is notable in that it selectively acts on the endosomal fraction of Vps34 but leaves autophagy undisturbed. Also, they uncover that a redox checkpoint is crucial for Vps34-dependent maturation of the endosome. The authors coin the term "triaptosis" to describe this new form of cell death promoted by redox-dependent depletion of endosomal PI(3)P (see the figure). Uncovering the function of triaptosis in cellular homeostasis and tissue biology will require further exploration. ■

IMAGES (FROM TOP): YU *ET AL.*; T. HU, *ET AL.*, *NAT COMMUN* 9, 2764 (2018) DOI: 10.1038/J.NATCOMMUN.2018.07017; DEVULAPALLI *ET AL.*

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MATERIALS SCIENCE

Distinct interfacial structures between grains

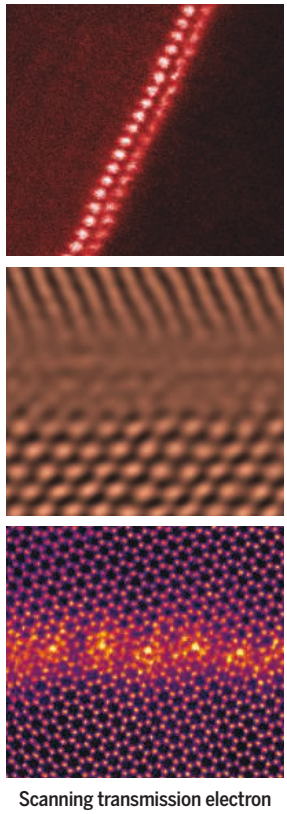
Adsorption transitions at grain boundaries in a polycrystal result in structures that are forbidden in bulk crystals

By **Jian Luo**[1,2]

Most solid materials are composed of small crystals (called grains) that comprise the same constituents but with different orientations within the polycrystal. Grain boundaries (GBs) form between two grains and control various properties. Adsorption of impurities or alloying elements at these interfaces can substantially alter a material's properties, such as strength and toughness. GB adsorption, also called segregation, can transform the structures and properties of an interface. Despite the importance of GB transitions in engineering materials, they are not well understood because of the challenges in characterizing structural transformations at the atomic level. On page 420 of this issue, Devulapalli *et al.* (*1*) report a detailed description of a GB transition in titanium that is induced by iron adsorption. It allows the formation of icosahedral structures that are forbidden in bulk crystals. The observation suggests new types of distinct interfacial structures and properties.

In 1968, first-order GB adsorption transitions were proposed (*2*) that were based on an extension of the Fowler-Guggenheim model for surface adsorption (*3*). This model can be derived by treating a GB as a regular solution (a solution model considering pair-wise interactions) (*4*). A first-order adsorption transition occurs when the effective regular solution parameter, Ω_{GB} (a measure of mixing enthalpy that is related to adsorbate-adsorbate interaction at the GB), exceeds $2RT$ (R is the gas constant and T is the absolute temperature) (*4*). This corresponds to a discontinuity in the slope of the GB energy versus bulk composition curve and a finite jump in the adsorption amount at the boundary, which was shown in a lattice model for nickel-bismuth (*5*). In addition, a GB transition can result in disinct interfacial structures such as an ordered bilayer in a nickel-bismuth alloy (*6*, *7*) or two types of disordered interfaces in a nickel-sulfur alloy (*8*).

In a broader context, GBs can be treated as two-dimensional (2D) interfacial phases, which are also called complexions to differentiate them from thin layers of bulk phases sandwiched between two grains (*4*). Such an interfacial phase is thermodynamically 2D because the structural and compositional profiles along the direction perpendicular to the GB are fixed (there is no degree of freedom in the third dimension) at the equilibrium. Such a 2D interfacial phase can have distinct structures that are neither observed nor stable in bulk phases. Consequently, they may possess properties unattainable by bulk materials.



Scanning transmission electron microscopy images show three types of two-dimensional interfacial phases: nickel-bismuth (top), nickel-sulfur (middle), and titanium-iron (bottom).

Devulapalli *et al.* report adsorption-induced transitions at a (nearly) symmetric tilt GB in a titanium-iron alloy by combining scanning transmission electron microscopy and atomistic simulations. They observed a GB structure with three subunits (A, B, and C) in an undoped titanium thin film. The authors systematically varied the amount of iron in titanium to study its role in the atomic arrangement at these GBs. Upon iron adsorption (segregation from the bulk material), Devulapalli *et al.* observed a transition from the ABC structure in polycrystalline titanium-iron alloy to one bearing icosahedral cages with fivefold symmetry. Such structural units are for-

bidden in a bulk crystal because they violate translational symmetry but can exist in glasses or quasicrystals. As the amount of iron doped into the titanium increased, the GB transited into a series of structures. These observations confirm a new type of 2D interfacial phases that have quasicrystal-like structures but are different from thin layers of quasicrystals. Devulapalli *et al.* described these transformations as topological GB segregation transitions, which are unrelated to the topological phases in condensed matter physics. Instead, these transformations indicate interfacial transitions that change the topological structure of the local bonding environment.

The results of Devulapalli *et al.* make an important contribution to the previously known cases of 2D interfacial phases at GBs. Atomic-level observations have shown periodically ordered bilayer adsorption of bismuth at GBs in a nickel-bismuth alloy (*6*). An adsorbed bismuth layer on each GB facet underwent reconstruction, which changed the 2D translational symmetry of each grain surface (*7*). For example, bismuth atoms adsorbed on (100) GB facets went through a c(2×2) reconstruction, in which the adsorbed atoms form a centered 2×2 supercell that was double the size of the underlying nickel grain surface (*7*). Another type of interfacial structures are amorphous-like intergranular films, which differ from their crystalline or amorphous bulk counterpart. These structures are much more disordered but still exhibit partial structural order, as shown in the 2D interfacial phase that is formed anisotopically on the (100) GB facets in a nickel-sulfur alloy (*8*). Similar liquid-like complexions can be formed by segregation-driven GB premelting (structural disordering at an interface below the bulk melting temperature) in binary alloys such as tungsten-nickel (*9*).

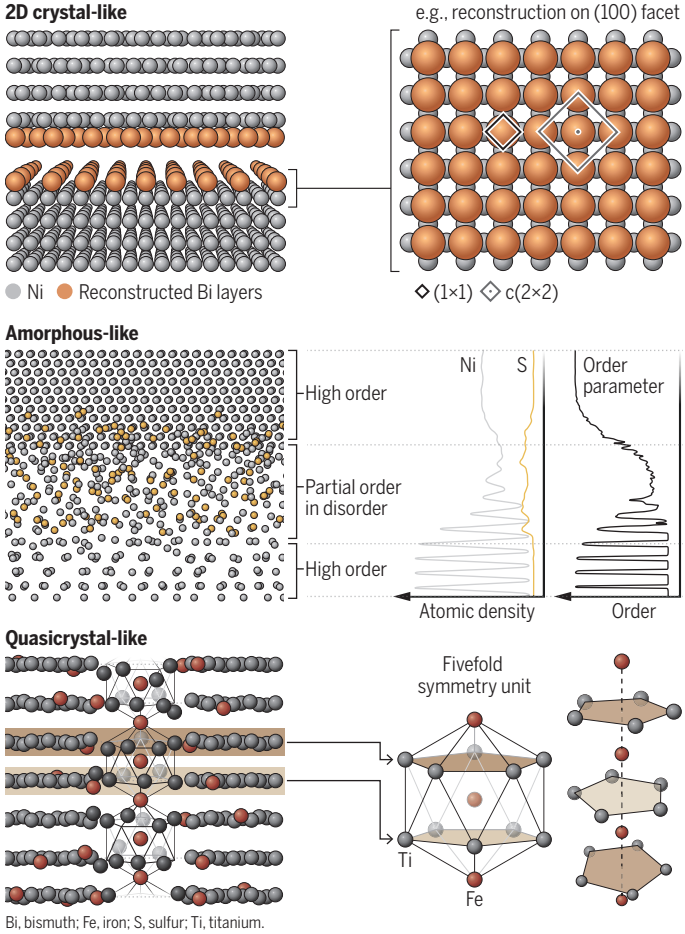
Based on the observations made to date, three classes of adsorption-based 2D interfacial phases have now been identified (see the figure). A 2D crystal-like GB contains highly ordered adsorbates, which change 2D translational symmetries of both grain surfaces. An amorphous-like boundary has a disordered interfacial structure with partial order within. A quasicrystal-like GB, revealed by Devulapalli *et al.*, can form from a new type of adsorption-driven 2D structural transition at an interface. Moreover, GB structural transitions can also take place without adsorption. A transition between domino and pearl motifs has been observed at a boundary in elemental copper (*10*). Thus, it would be interesting to also investigate GB transitions that occur with changes of other conditions such as temperature and pressure.

Further studies should investigate whether 2D interfacial phases based on icosahedral cages form broadly at other types of GBs and in different materials and the resulting properties. In general, studies of GB phase-like transitions have helped resolve decades-old mysteries in materials science, such as the atomic-level origins of liquid-metal embrittlement (*6*, *7*), activated sintering (*9*), and abnormal grain growth (*4*, *11*). For example, ordered (*6*, *7*) and disordered (*8*) 2D interfacial phases have been shown to cause embrittlement in nickel-bismuth and nickel-sulfur, respectively, which are two classical GB embrittlement systems in physical metallurgy. Analogous to using 2D surface phases to improve the functional properties of battery materials (*12*), the 2D interfacial phases at GBs can potentially be engineered to achieve exotic properties, such as superior ionic conductivity.

Given that bulk phase diagrams are arguably the most useful tool in materials science, computing GB phase diagrams can be equally important (*13*). In addition to the common thermodynamic potentials such as temperature, chemical potentials, and pressure, GB transitions can also be driven electrochemically by applying electric fields to alter the microstructural evolution of an oxide (*14*). Because adsorption at the boundary results in more diverse 2D interfacial phases in alloys with multiple elements than in unary (one-component) systems, it will be fascinating to further investigate the GB transitions in multicomponent and high-entropy alloys, including the emerging concept of high-entropy GBs (*15*). ■

Adsorption-induced interfacial transitions

Adsorption of impurities or alloying elements can result in various types of structural transitions at grain boundaries. Quasicrystal-like boundaries in titanium-iron alloy form fivefold symmetry units, contributing to the previously known cases of two-dimensional (2D) interfacial phases.



Bi, bismuth; Fe, iron; S, sulfur; Ti, titanium.

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