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Grain boundary plane manipulation in directionally solidified bicrystals and tricrystals

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We report a novel crystal growth technique for manipulating the grain structure of directionally solidified bicrystals, tricrystals, and other higher order oligocrystals. Controlling both the direction of local heat flux and the thermodynamic forces acting on the grain boundary, we can continuously vary grain boundary position and orientation, a level of control not possible using traditional processing strategies. This processing method can now specify many combinations of the five crystallographic grain boundary parameters in a single specimen, meaning large portions of both the grain boundary and triple junction parameter spaces can be sampled quickly and efficiently.

Grain boundaries are two-dimensional crystallographic defects between misoriented grains in polycrystalline materials and an important factor in many material properties. Decreasing the grain size in a material, and therefore increasing the total area of grain boundaries, can increase yield strength [1] and fracture toughness [2]. However, grain boundaries can also degrade material performance, acting as preferred sites for stress corrosion cracking [3], liquid metal embrittlement [4], and solute segregation [5,6]. The properties of a grain boundary are linked to its crystallography, which is described by five macroscopic degrees of freedom: three describe the misorientation between the neighboring grains and two describe the grain boundary plane orientation. It is possible to optimize the properties of a material by manipulating the types of grain boundaries it contains through a process termed grain boundary engineering (GBE). In GBE, repeated cycles of plastic deformation and annealing are used to increase the concentration of coincidence site lattice boundaries, which have specific misorientations and attractive properties like improved corrosion resistance [7–9]. However, efforts to create optimal grain boundary networks through GBE have been hindered by (i) a lack of direct control over both grain boundary character and position in materials, and (ii) an incomplete understanding of grain boundary structure-property relationships.

A major challenge in establishing grain boundary structure-property relationships lies in the scale of the five-dimensional grain boundary parameter space. For example, approximately 6500 unique bicrystals, each having a single combination of the five grain boundary parameters, are required to completely map the grain boundary parameter space for a high symmetry face-centered cubic metal like copper [10]. Growing and characterizing this many bicrystals is, of course, not practical. Historically the approach to this problem has been to study many boundaries simultaneously by characterizing cross sections of polycrystalline materials or by using techniques like serial sectioning [11,12] and three-dimensional X-ray diffraction [13–15], which can measure the complete grain boundary character distribution. These high-throughput techniques can only sample the entire grain boundary parameter space if they are applied to specimens with a grain boundary character distribution that sufficiently represents the space, which is never the case in conventionally processed materials. There is thus a need for processing techniques that can create specimens that efficiently sample the grain boundary parameter space. In this work, we address this challenge by demonstrating a technique for growing oligocrystals (i.e., polycrystals containing few grains) with prescribed grain structures.

Many of the early studies on grain boundaries used bicrystals consisting of two misoriented grains that meet to form a single flat grain boundary. These planar bicrystals are typically grown using directional solidification, with the orientation of each grain controlled by seed crystals [16]. Fleischer and Davis showed that it is possible to suppress grain boundary migration during this growth process by using molds with a cross section like that shown in Fig. 1A [17]. Here the grain boundary terminates on sharp cusps, which pin the boundary at its edges, much like thermal grooves pin grain boundaries in thin films [18]. Decreasing the included angle (θ) and separation (δ) of the cusps increases the stability of the pinned grain boundary.

In the present work we leverage this pinning effect to grow geometrically complex bicrystals using molds where the positions of the cusps twist and oscillate along the length of the mold. These molds would be difficult to fabricate with traditional manufacturing methods. Instead we prepared them using a hybrid 3D printing technique originally

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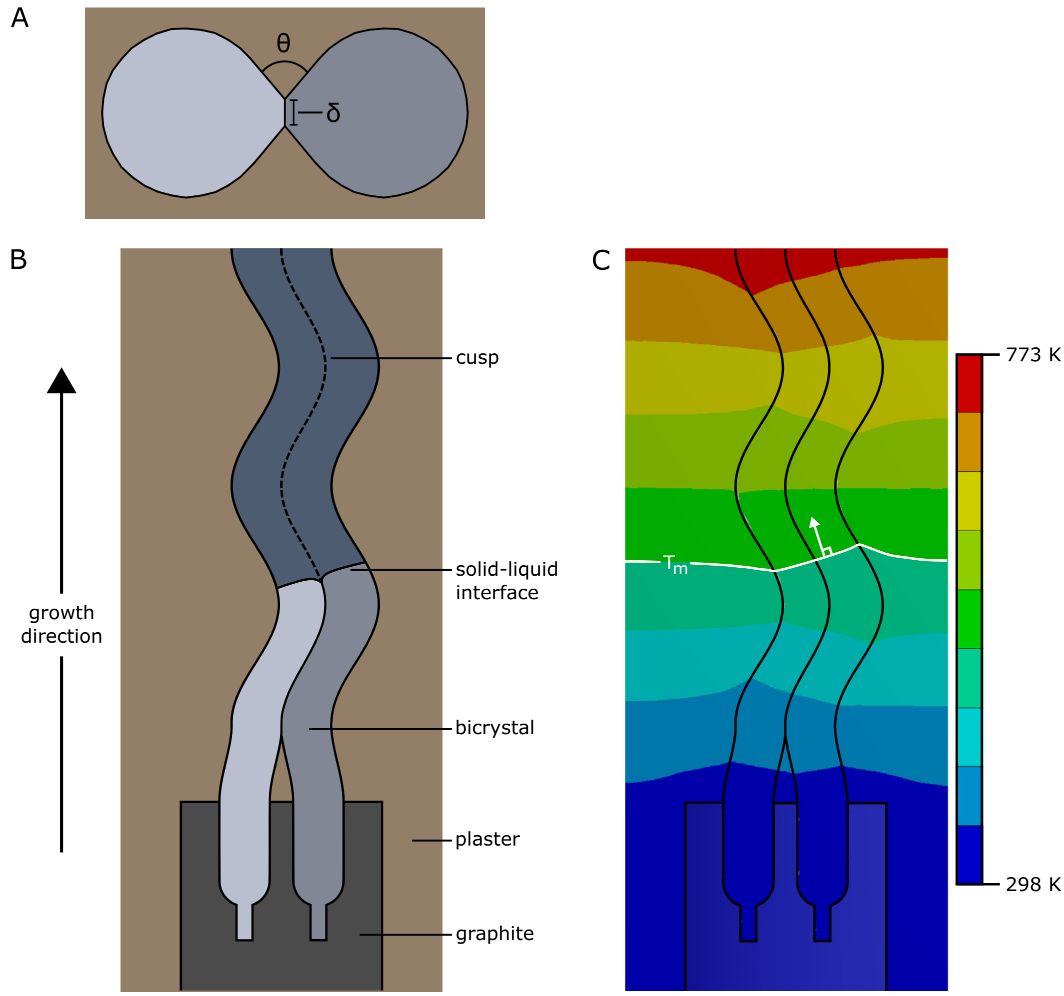

Fig. 1. Mold for sinusoidal bicrystals. (A) Transverse cross section of the bicrystal mold, showing the included angle θ and gap between the cusps δ. (B) Longitudinal cross section of the mold used to grow sinusoidal bicrystals, shown during crystal growth. Each grain is distinguished by a different color. A graphite chill is placed at the base of the mold to aid heat transfer. (C) Finite element analysis of the steady state temperature profile in the mold and metal charge during solidification. The isothermal contour highlighted in white corresponds to the melting point of tin (505 K). Note that the normal direction of the solid-liquid interface is tilted away from the macroscopic growth direction and is nearly parallel with the cusp.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

developed for rapid prototyping of castings [19]. We first printed a poly (methyl methacrylate) positive of the bicrystal using a Formlabs stereolithography printer. Next we attached the pattern to a graphite chill and invested the whole assembly in plaster of Paris (Plasticast™, Ransom and Randolph). Lastly we removed the 3D-printed positive from the mold by burning it out. A bicrystal growing in one of these 3D-printed molds is depicted in Fig. 1B. The graphite chill at the bottom of the mold helps maintain a steep temperature gradient in the melt, encouraging plane-front solidification and suppressing nucleation of stray grains.

Although the cusps exert a strong pinning force, the grain boundary can still de-pin if the cusps intersect the melt at a non-normal incident angle. This is because the torques acting on a grain boundary in contact with the melt will tend to orient the grain boundary perpendicular to the solid-liquid interface [20]. This tendency to de-pin can present a challenge when growing bicrystals in molds like the one shown in Fig. 1B, where the cusps are rarely parallel to the applied uniaxial temperature gradient. Importantly, we found that it is possible to design molds such that the solid-liquid interface remains nearly perpendicular to the cusps even when the cusp path is not parallel with the applied temperature gradient. Fig. 1C, for example, shows results from a finite element simulation of the pseudo-steady state temperature profile during the growth of a tin bicrystal in a plaster mold. The macroscopic temperature gradient is uniaxial, with fixed temperature boundary conditions at the top and bottom of the mold. However, inside the metal charge, the isothermal contours tilt so that they remain almost perpendicular to the cusps. Additional finite element simulations included in *Supplementary Material* show that this effect results from the high contrast in thermal conductivity between the metal charge and the plaster mold.

The combined effects of grain boundary pinning and local temperature gradient manipulation enable growth of new bicrystal designs in which boundary plane orientation varies continuously along the length of the bicrystal. The first new design is a bicrystal where the cusps oscillate along the growth direction, like the sinusoidal bicrystal in Fig. 2A. In this example bicrystal, the grain boundary plane normal vector traces a 65° vertical arc, shown in green in Fig. 2D, a partial unit sphere representation of the angular range of the grain boundary plane. The second design is a bicrystal where the cusps rotate about the central axis of the specimen, like the helical bicrystal in Fig. 2B. In this bicrystal, the boundary plane normal traces a 90° azimuthal arc, shown in red in Fig. 2D. In each of these new bicrystal designs, one of the two grain boundary plane degrees of freedom varies while the other, and the misorientation, remain constant.

To demonstrate this crystal growth strategy, we used 3D printed molds to grow geometrically complex bicrystals from nominally pure tin (99.9%). We performed the growths in air using a Bridgman furnace with a temperature of 773 K and velocity of 2.5 cm/h. Examples of the geometrically complex bicrystals are presented in Figs. 3 and 4. Fig. 3A