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Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

The influence of alloying in stabilizing a faceted grain boundary structure

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ARTICLE INFO

Article history: Received 2 June 2020 Revised 14 August 2020 Accepted 28 September 2020 Available online 3 October 2020

Keywords: Grain boundary structure Grain boundary segregation HRTEM Faceting Platinum-alloys

ABSTRACT

Grain boundary structures have long been known to depend on factors such as solutes and temperature. In this work, *in-situ* atomic scale imaging was used to observe the faceting of a $\Sigma 21a$ [111]-tilt-axis boundary at 600 °C and 800 °C in a Pt-5Au (at. %) nanocrystalline alloy. With an increase in temperature, we observe an evolution from many, shorter facets to fewer, longer facets. The preferred facets are shown to be symmetrically equivalent tilt boundaries, via the fundamental zone formalism. Simulation of Pt bicrystals reveals that these preferred facets do not lie in an energy minimum (of the tilt boundaries that the grain boundary misorientation could access); however, calculation of the segregation enthalpy of Au to these grain boundary lattice sites indicates a greater preference of Au, reducing the grain boundary energy, and explaining the facet stabilization observed.

ary plane [14–16].

via symmetry operators.

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rigid adherence of the atomic structure to the theoretical bound-

be used to ensure that each grain boundary is defined in a unique

manner. For example, accounting for symmetry allows for the

identification of equivalent facets. A useful formalism was devel-

oped by Patala and coworkers [8,9] for describing unique grain

boundary misorientations and boundary planes. This formalism

develops regions of both the misorientation and boundary plane

spaces that contain only unique misorientations and boundary

planes, respectively. Misorientations and boundary planes that are

outside these fundamental zones may be mapped into these zones

metry of the space it is meant to describe. For misorientation fun-

damental zones, the crystal structure of the grains informs their shape, which is three-dimensional. For boundary plane fundamen-

tal zones, the misorientation and the crystal structure control the

scope of the two-dimensional zone. If two or more points (e.g.

boundary planes) map to the same location in the appropriate fun-

damental zone, those points are said to be symmetrically equiva-

lent. The interested reader is referred to the literature [8,9] for fur-

ther details on the mathematical development of the fundamental zone formalism, with the development of the boundary plane fun-

The boundary plane fundamental zone allows us to discover similarities in crystallography and properties that otherwise might not be readily identifiable. Properties have already been shown

damental zone used in this work provided in Appendix A.

The geometry of the fundamental zone depends on the sym-

The symmetry inherent with crystals and grain boundaries may

1. Introduction

Grain boundaries are technologically important defects that strongly influence many material properties. For example, the average grain size effects strength [1–4], ductility [3,4], fracture toughness [4], and electrical resistivity [5]. The influence of grain boundaries on properties arises from the two-dimensional interruption in the crystalline lattice, hindering propagation of dislocations and electrons [6,7].

From a crystallographic standpoint, a grain boundary is defined by three macroscopic degrees of freedom for the misorientation between the grains [8] and two macroscopic degrees of freedom for the boundary plane [9]. An additional six microscopic degrees of freedom-to account for factors such as miscellaneous positioning of the two lattices with respect to one another, boundary plane position, and atom proximity at the boundary-exist too [10,11], but are generally neglected for reasons described elsewhere [10–13]. These microscopic factors are important for finding the minimum energy structure in atomistic simulations.

Although each grain boundary has a defined plane at which the two crystallites intersect, the atomic structure of the boundary may not strictly follow this theoretical plane. If this is the case, the grain boundary may approximate the theoretical plane with two or three low energy planes. This is known as faceting and allows the grain boundary to achieve a lower energy configuration than

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https://doi.org/10.1016/j.actamat.2020.09.085

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to vary smoothly when presented within the fundamental zone framework. Homer et al. reported that simulated nickel grain boundary energies varied smoothly within the boundary plane fundamental zones for several different misorientations (including along different misorientation axes) [11].

Models for describing the energetic landscape of the boundary plane fundamental zone have used faceting to describe grain boundary structure and obtain estimates of interfacial energy. Banadaki and Patala devised a model in which $\Sigma 3$ grain boundaries in Al were approximated by appropriate combinations of the three low-energy boundary planes ((1 1 1),, (2 $\overline{1} \overline{1}$), and (1 0 $\overline{1}$)) bounding the $\Sigma 3$ boundary plane fundamental zone [17]. Using this approximation, they were able to predict simulated $\Sigma 3$ grain boundary energies across the entire boundary plane fundamental zone with some accuracy. Although examining the atomic structure was not a focus of Ref. [17], a follow-on paper [18] showed that the atomic structures of these boundaries are often well represented as having components of the three low-energy planes.

This is not to suggest that all grain boundaries, save those of the lowest energy, will have their boundary planes approximated by the combination of other boundary planes (i.e. facet). Indeed, depending upon the temperature, a grain boundary may transition between a faceted and flat, or de-faceted, structure. Hsieh and Balluffi reported reversible transitions between faceted and de-faceted structures in Al (Σ 3 and Σ 11) and Au (Σ 3) boundaries when those structures are heated close to the melting temperature and then cooled [14]. Lee et al. reported similar reversibilities for a Σ 5 grain boundary in SrTiO₃ [15].

The energetic landscape of grain boundaries may be modified by the introduction of solutes, with reports of faceting/de-faceting transitions occurring as the solute is introduced and then removed from the grain boundary, such as Bi solutes in a Cu boundary [19]. The opposite has also been reported. A recent atomistic study by O'Brien et al. showed that an initially faceted $\Sigma 21b$ ([211] 44.4°) ($\overline{1}$ 0 $\overline{3}$) grain boundary in Pt lost the faceted structure with the introduction of Au [20]. While seemingly contradictory, these behaviors are compatible, as segregation to grain boundaries (and faceting transitions) depend on many factors, including the crystallography of the boundaries as well as the chemical species involved.

Segregation may also be favorable to specific sites. In Fe-Cr, the Cr grain boundary segregation has been shown to be highly dependent on the grain boundary structure, using both experiments and simulations [21]. Wagih and Schuh simulated the enthalpy of segregation of Mg atoms in an Al polycrystal and found that the segregation enthalpies formed a spectrum [22]. Further analysis of the segregation enthalpies to different grain boundary atomic sites revealed that the high and low enthalpy values were dispersed amongst all grain boundaries, although the relationship between grain boundary crystallographic structure and the segregation enthalpies was not explored.

With regards to faceting, work by researchers at the Max-Planck-Institut für Eisenforschung (MPIE) has shown that segregation to faceted grain boundaries can be concentrated to specific defects. Liebscher et al. examined C and Fe solute segregation in $\Sigma 3^n$ faceted Si grain boundaries and found that the solutes that had segregated to the boundaries preferred one type of facet junction (over the other facet junction and general facet regions) [23]. Peter et al. investigated Ag solute segregation to $\Sigma 5$ Cu grain boundaries. Here the unalloyed boundaries had very small facets, while the doped boundaries had a much stronger faceting character. Furthermore, the solute preferred specific sites within one facet type that produced an atomic structure transition in those facets, while the other facets had weak preference for Ag [24].

In this work, we conduct an *in-situ* anneal of a Pt-Au alloy while observing a grain boundary using an aberration-corrected,

high-resolution transmission electron microscope. We observe the structural evolution of this grain boundary in response to exposure to 600 °C and 800 °C. The Pt-Au system is selected for 1) noble metal constituents, avoiding any confounding factors associated with oxidation [25-27] and 2) proven partitioning of Au to Pt boundaries, via studies of nanocrystalline stability [20,28]. The use of *in-situ* annealing allows the structure of the grain boundary to be captured as it evolves, rather than only capturing the endstate, as would occur with an *ex-situ* study. This *in-situ* capability is particularly relevant because the grain boundary accesses a series of configurations of strong faceting. Drawing on the direct atomic images we collected, the facets are described using the boundary plane fundamental zone, which reveals the occurrence of symmetric equivalents in the boundary. We also conduct atomistic simulations to clarify the reasons for this faceting, including the influence of solute on the energetics of faceting.

2. Methodology

The Pt-5Au (at. %) nanocrystalline alloy was synthesized as a thin film by magnetron co-sputtering in an AJA ATC 1500 sputtering system that has a base pressure below 1.33×10^{-5} Pa. Ultrahigh purity Ar gas was flowed into the chamber to a pressure of 0.267 Pa and served as the working gas for the plasma. The Pt and Au targets are each 99.99% purity and were set at powers of 120 W and 40 W, respectively, to achieve the targeted alloy composition. The film was deposited onto a DENSsolutions (Delft, Netherlands) Wildfire *in-situ* annealing chip at a rate of approximately 3.0 Å/s to achieve a total film thickness of 15 nm (nominal).

The sample was characterized in a ThemIS aberration-corrected transmission electron microscope at the National Center for Electron Microscopy at the Molecular Foundry within Lawrence-Berkeley National Laboratory. This microscope was operated at an accelerating voltage of 300 kV in high-resolution mode (no objective aperture) to provide direct atomic imaging of the nanocrystalline structure. The sample was heated at a nominal rate of 3 °C/s to 600 °C. After twenty-two minutes, the temperature was ramped at a nominal rate of 3 °C/s to 800 °C and held.

Using the collected high-resolution images, the orientations of the grains were determined via fast Fourier transformations (FFT) of the imaged atomic structures. These transformations allow us to access reciprocal space and serve as 'pseudo'-diffraction patterns that are indexed and analyzed to yield the orientation of the grain. Note that the FFT was applied to image regions corresponding to a single grain. Grain boundary profiles were manually identified from each high-resolution micrograph with each segment of these profiles characterized using the boundary plane fundamental zone formalism developed by Patala et al. [8,9].

Atomistic simulations were executed using LAMMPS [29], on University of Alabama High Performance Computing systems. These simulations used the PtAu embedded atom method potential developed by O'Brien et al. [20]. A set of Σ 21a [111]-tilt-axis grain boundaries were constructed as bicrystal simulation cells using the methodology of Homer [30] (itself adapted from Olmsted et al. [10]). These simulation cells are periodic in the dimensions of the boundary plane and non-periodic in the direction of the boundary plane normal, producing a single grain boundary. The non-periodic dimensions produce two free surfaces parallel to the boundary plane at each end of the simulation cell. Like Olmsted et al., atoms within a given distance of the free surface (approximately 8 Å in this work) were constrained to move as a block to prevent surface relaxation. These block atoms are not included in the energy calculations, and lie at least 85 Å away from the nearest grain boundary atoms. A series of starting configurations for each bicrystal are generated (that account for the six microscopic degrees of freedom). The atomic structure of each starting

configuration was minimized using the conjugate-gradient method, with energy and force tolerances of 10^{-10} (energy change/energy magnitude) and 10^{-10} eV/Å, respectively. The global minimum energy structure after minimization is taken as the minimum grain boundary structure for that bicrystal.

The segregation enthalpy spectrum was determined using the methodology employed by Wagih and Schuh [22], in which the identity of a single atom in the simulation cell was changed from Pt to Au with the simulation cell structure then minimized with respect to energy. The segregation energy of an Au atom to the ith grain boundary site is taken as the difference in energy of the simulation cell when the atom is at a bulk site and at the *i*th boundary site. A bulk site must be at least 3 nm away from nonface-centered-cubic atoms (such as those at free surfaces and grain boundaries). By repeating this procedure for all *i* grain boundary sites, we produce a list of segregation enthalpies of Au to the grain boundary. Because the simulation cell is held at zero pressure and 0 K, the segregation energy reasonably approximates the segregation enthalpy. Our tolerances on the conjugate gradient minimization for each substitution are 10⁻¹⁰ (energy change/energy magnitude) and 10^{-10} eV/Å for the energy and force, respectively. As we are attempting to explain experimental observations, we determine the segregation enthalpy spectrum for each simulated bicrystal in order to evaluate the thermodynamics of segregation on a per-boundary basis.

3. Results and discussion

3.1. High-resolution micrographs with faceted boundary

High-resolution transmission electron micrographs of the experimental grain boundary during the *in-situ* annealing are shown in Fig. 1. The microscopy images are plotted in rows corresponding to temperature: 600 °C and 800 °C. These are representative micrographs from a collection of images taken at these temperatures and times. In Fig. 1, we can see that the grain boundary has a particular faceted form, making it of interest. Furthermore, its

preference for faceting coupled with an apparent approximation to a curved boundary (rather than to an approximate flat boundary plane) adds additional peculiarities. As annealing time and temperature increase, the grain boundary profile evolves. We observe significant changes with the temperature increase from 600 °C to 800 °C, from many shorter facets to fewer, longer facets.

3.2. Preferred facets are symmetric equivalents

As the grain boundary evolved, specific facets appeared to be preferred. To understand this behavior, we examine the crystallography of these facets. Fig. 2 is a visual guide to our explanation of the crystallography developments of the grain boundary during annealing. First, we determine the misorientation between the two grains. Since we have a high-resolution image in which both grains are on a (111) zone axis, we apply a Fourier transform to regions of the image that correspond to a single grain ("FFT1" and "FFT2" in Fig. 2(a)). The minimum rotation about a $(1 \ 1 \ 1)$ axis to bring the two crystals into alignment with each other is ~22.5°, which approximates the $\Sigma 21a$ ([1 1 1] 21.8°) misorientation. When this FFT procedure is repeated for the final 800 °C image, the excited 220 reflections from the FFT of the final image fall within the circles marking those reflections obtained from the first image (Fig. 2(a)). These similarities in grain orientations at beginning and end lead us to assume that the grain boundary misorientation is constant during the experiment.

Given the 15 nm nominal film thickness and our ability to resolve atomic columns in the immediate vicinity of the boundary, then the boundary planes are parallel to a [1 1 1] viewing axis. Therefore, all boundary plane normals in this Σ 21a interface must have Σ 21a [1 1 1]-axis tilt character. The unique [1 1 1]axis tilt boundary planes are identified with a color gradient along the outer "arc" of the Σ 21a boundary plane fundamental zone in Fig. 2(b). The angle α controls the sweep from $-\frac{\pi}{6}$ to 0 for these tilt grain boundaries. There is two-fold rotational symmetry about the [5 $\overline{4}$ $\overline{1}$] axis, so the upper portion of the outer arc is symmetrically equivalent to the bottom portion. For more details on the Σ 0



Fig. 1. High-resolution transmission electron imaging of the studied grain boundary. The images increase in time from left-to-right and then down.



Fig. 2. An examination of the crystallography of the studied Σ 21a grain boundary. (a) is a high-resolution transmission electron micrograph collected during *in-situ* annealing. The regions of the micrograph on which fast Fourier transforms were performed are marked, and these transforms are shown to the right of the micrograph. The excited 220 reflections are marked with black circles. (b) is the boundary plane fundamental zone for the Σ 21a misorientation. The vertices of this zone are marked (e.g. (1 1 1)). The inclination angles α and β required to achieve a given (*h k l*) plane within this fundamental zone are shown. The [1 1 1]-axis tilt grain boundaries of this zone are found on the outer arc (between (5 $\overline{4}$ $\overline{1}$) and (2 $\overline{3}$ 1)); a color gradient for these tilt grain boundaries is provided that varies with α . (c) presents the profiles for the studied grain boundary; the segments of these profiles are colored according to the color scheme presented in (b). The profiles are grouped according to the temperature at which they were recorded, and time increases from left to right. The black dashed lines are approximate curved boundaries for each profile; the black dotted line on the left-most curve represents a planar boundary (not plotted on subsequent profiles for clarity). (d) is a histogram of the inclination angles α observed from (c), according to segment fractional length. The preferred facet range is marked.

21a boundary plane fundamental zone construction, the interested reader is referred to Appendix A and Refs. [9,11].

The temporal evolution of this $\Sigma 21a$ grain boundary is plotted with respect to increasing time in Fig. 2(c). The segments of each temporal profile are colored according to their position in the boundary plane fundamental zone (e.g. dark blue denotes boundary planes near the $(5 \overline{4} \overline{1})$ boundary plane normal). The temporal profiles are horizontally offset from one another for clarity; this offset is not meant to convey grain boundary migration. Each temporal profile is anchored by its lower end, as it is difficult to consistently position the profiles vertically due to the evolving conditons of the surrounding microstructure. For each profile, we plot an arc as a black dashed line to approximate the ideally curved boundary, based on the shape of the experimentally observed boundary. This arc is fixed at the grain boundary endpoints (triple junctions) and uses the radius to search for a best fit to the profile. We also plot the ideal planar boundary (dotted line) between the triple junctions for the first profile to highlight the difference between a curved boundary and a planar boundary.

In Fig. 2(d), we plot a histogram of the [1 1 1]-axis till boundary character (via the inclination angle α), with respect to length fraction over all profiles. From this histogram, we observe that there is a clear preference for a particular facet ($\alpha \approx -\frac{3\pi}{64}$). The principal finding from Fig. 2 is that the grain boundary prefers to facet, and that the preferred facets are symmetric equivalents, both by

visual inspection of Fig. 2(c) and the preference for a particular tilt boundary character per Fig. 2(d).

3.3. Grain boundary profile approximates a curved boundary

The grain boundary profiles do not appear to approximate a flat plane, as there is significant deviation of the boundary profiles from a line connecting the triple junctions (ends of the profiles). Rather, visual comparison of the curved trajectories marked in Fig. 2(c) to the profiles themselves suggests that the faceted structure arises to minimize the grain boundary energy while approximating a curved grain boundary. Faceting to approximate a curved interface ('curved' faceting) has been reported by Hsieh and Balluffi in a Au Σ 3 boundary[14], as in this work here. Curved faceting represents a distinct faceting behavior from the typically observed 'planar' faceting. The major difference between these two faceting modes (curved vs. planar) lies in the ability to use symmetrically equivalent facets. Whereas a flat boundary must alternate between different facet planes (i.e. $(1 \ 1 \ 1)$ and $(2 \ \overline{1} \ \overline{1})$, see Refs. [14,15,17,20,24,31]), a curved boundary can use symmetrically equivalent facets (i.e. $(1\ 1\ 1)$, $(\overline{1}\ 1\ \overline{1})$, see Ref. [14]).

3.4. Facets are 60° from each other

While symmetrically equivalent facets may occur in a curved boundary, not all possible equivalents may be used. In Fig. 2(c) we



Fig. 3. Schematic depicting the concept of extra facets. On the left, a portion of the stereographic projection of the Σ 21a boundary plane space is presented. The approximate location of the preferred facet is shown as a large red circle outlined in black. The other plotted circles (both red and blue) are symmetric equivalents; the color distinguishes the two symmetric equivalents belonging to the dashed or solid portions of the outer arc. Despite the occurrence of a symmetric equivalent boundary plane normal at alternating intervals of ~16° and ~44°, the grain boundary selects facets at intervals of 60°. This means that there are symmetrically equivalent facets that do not appear in the structure. These are shown in the profiles on the right, where the color represents the "symmetry" of the facet and the dashed lines represent the boundary plane normals that do not appear.

observe that the facets are approximately 60° from each other. This is not the smallest possible angle between symmetrically equivalent [1 1 1]-axis asymmetric tilt facets for Σ 21a. Fig. 3(a) contains a portion of the boundary plane sphere (Fig. A.7). The approximate location of the preferred facet is plotted as a large circle outlined in black; symmetric equivalents are plotted as smaller circles outlined in gray. Equivalent boundary planes that are on the "symmetric" arc of the fundamental zone are colored blue to differentiate them from the unique portion of the outer arc (red). This symmetric portion of the outer arc arises because of two-fold rotational symmetry about axes such as the $[4\ 1\ \overline{5}]$, $[5\ \overline{4}\ \overline{1}]$, and $[1\ \overline{5}\ 4]$. From Fig. 3(a), it can be observed that there are two different steps between symmetrically equivalent facets, of approximately 16° and 44°. Despite this pattern of symmetrically equivalent boundary planes, the preferred facets differ in angle by approximately 60°, in other words, skipping every other possible facet.

We highlight the additional possible facet orientations in Fig. 3(b), wherein a schematic of the observed faceting behavior is marked with solid lines. The alternate facets are plotted as dashed lines. Though the reasons for this behavior are unknown, it may be possible that the intersection of the preferred equivalent facets at 16° and 44° is at a higher energy and/or are more mobile. The idea that the 60° intersections are very low in energy is bolstered by the persistence of 60° sharp intersections to a temperature of 800° C.

3.5. Evolution of Σ 21a faceted grain boundary structures

At 600 °C, the boundary has more, shorter facets than at 800 °C (Figs. 1 and 2). The shape of the boundary does not significantly change when held at 600 °C, although there is some increase in the distance between the triple junctions, which indicates that there is some migration in the neighboring grain boundaries. However, af-

ter the ramp to 800 °C, we observe that the grain boundary profile changes significantly, with the first 800 °C profile in an apparent non-equilibrium state. The return to (near-)equilibrium in subsequent profiles sees the grain boundary having fewer, longer facets than at 600 °C. The preferred facet does not appear to change as a result of temperature, in other words, the majority of profile segments in Fig. 2(c) remain blue rather than shifting to dark blue, green, or yellow.

With the increase in temperature to 800 °C, the top portion of the grain boundary also develops a long "tail", with the triple junction migrating to the left compared to previous profiles (Fig. 2(c)). However, as time progresses, this so-called tail shortens, moving back to the right. This triple junction motion appears to be in response to migration of neighboring grain boundaries, especially with respect to the elimination of nearby grains. Fig. B.8 (in Appendix B) contains larger area-of-view micrographs capturing these microstructural changes. As the tail evolves, the preferred facet emerges. However, the facet junction in the tail does not achieve a sharp configuration, instead it remains curved. Despite this curvature, the tail facet intersection does not manifest any significant migration to alleviate this arc (i.e. the increase in its radius of curvature).

3.6. Preferred facets are energetically favored with increasing Au segregation

We now seek to explain the preferred faceting behavior. To do so, we used molecular statics simulations to extract the minimum energies of $\Sigma 21a$ tilt grain boundary bicrystals as well as estimate the segregation enthalpy spectrum for each grain boundary. We present the thermodynamic results in Fig. 4. Fig. 4(a) plots interfacial energies (γ_{GB}) vs. inclination angle α for the pure Pt bound-



Fig. 4. Σ 21a tilt grain boundary energies. (a) is a plot of the interfacial energies of pure Pt boundaries at 0 K as determined by molecular statics, plotted against their boundary plane inclination angle α . (b) is a plot of the distribution of segregation enthalpies for Au to Pt grain boundaries, also calculated by molecular statics. (c) plots the estimated grain boundary interfacial energy (at 0 K) in Σ 21a [1 1 1]-axis tilt grain boundaries at various fractions of Au solute (steps of 0.05 Au) at the grain boundaries (in increments of 0.05). The dashed line represents the approximate location of the preferred facets observed from the *in-situ* work (see Fig. 2). (d-f) are gamma plots for the expected grain boundary faceting for Pt-xAu, where x = 0, 10, and 25 at. %, respectively. These plots are generated from the data plotted in (a) and (c), and are used to find the equilibrium shape of the crystal surface (interface) for Σ 21a [1 1]-axis tilt grain boundaries. The concentric rings indicate γ_{CB} in mJ/m²; all three plots are scaled identically and omit a ring each for clarity.

aries at 0 K. This plot indicates that the $(5 \ \overline{4} \ \overline{1})$ boundary is the minimum energy for the $\Sigma 21a$ tilt grain boundary at 0 K.

Thus, we now consider the influence of Au on interfacial energy and the thermodynamics of faceting. Fig. 4(b) contains the segregation enthalpy distributions of the atomistic grain boundaries. These distributions are plotted as cumulative summations of the number of atom sites (normalized by the grain boundary area) against the segregation enthalpy of a Au atom to a grain boundary atomic site. Although the units should strictly be in eV/site on the abscissa, we opt to present the data in units of kJ/mol to facilitate comparison with other published work describing enthalpies of segregation [22,32–34]. The grain boundaries are colored according to the same color gradient used to color the grain boundaries in Fig. 2; this color gradient is repeated in the upper left corner. From Fig. 4(b), we can see that grain boundaries have similar segregation enthalpy distributions in terms of shape if not magnitude. In other words, for the $\Sigma 21a$ [1 1 1]-tilt-axis grain boundaries, high and low segregation enthalpy sites are to be found on all grain boundaries, with no grain boundary exerting a monopoly on any particular segregation enthalpy range. Wagih and Schuh reported (qualitatively) a scattering of segregation enthalpies amongst all grain boundaries, so these results are in agreement with the literature. While every grain boundary has a similar mix of positive and negative segregation sites, some grain boundaries have more sites per unit area than others. These interfaces can therefore lower their energy further than boundaries with fewer sites.

Based on the segregation curves of Fig. 4(b), we can determine an alloyed grain boundary energy (γ_{GB}) for each simulated grain boundary (see Appendix C). These interfacial energies are plotted in Fig. 4(c), with the alloyed grain boundary energy (γ_{GB}) plotted against the boundary plane inclination angle α . In Fig. 4(c), we plot the interfacial energies for several fractions of Au occupying the atomic positions of the grain boundary; these curves are plotted according to the color scheme shown at the top of the figure. The approximate location of the preferred facet is marked with a dashed line. From these curves, we can see that the grain boundary energy can be significantly lowered through segregation of Au to the interface, with preference for the near-preferred tilt boundaries (facets). Though the dashed line in Fig. 4(c) does not reside in the absolute minimum energy location, it resides near it and we will return to explaining this modest shift in Section 3.8.

Experimentally, this boundary is pinned by two triple junctions. To determine how the faceting would evolve in a general condition, we have generated a series of gamma plots (following the Wulff construction) for undoped and doped boundaries. These are shown in Fig. 4(d–f). In each plot, concentric iso-energy (γ_{GB}) rings are marked, with the faceted boundary structure plotted from the energy data of Fig. 4(a,c). The plotted circles represent the interfacial energies of the grain boundaries at the specified inclinations. The predicted, favorable facet forming inclinations are plotted as red filled circles, while blue open circles would be predicted to facet using the inclinations of the red circles.

In the un-doped Pt boundaries, the equilibrium shape (around the entire circle) is approximately a hexagon with slightly blunted edges. Given this shape, we estimate that an un-doped faceted configuration would have major segments ($\alpha = 0$) and minor segments ($\alpha = -\frac{\pi}{6}$).

By adding Au to the boundary, the faceting behavior drives the system towards a single inclination evident by the symmetricallyequivalent, twelve-sided shape. The symmetric equivalents of this preferred facet makes the shape now approximate a circle. These gamma plots reveal that the experimentally observed faceting is accessible in pinned and unpinned conditions. This estimated equilibrium shape for doped boundaries relates to the discussion of missing facets (Fig. 3), in that there are predicted facet planes that do not appear.

The relative maximum difference between the grain boundary energies remains the same, i.e. approximately 100 mJ/m². However, the lowest energy (alloyed) tilt boundaries are those that are near the preferred facet orientation. Although the model does not account for temperature, a simulation study in the Fe-Cr system has reported good prediction of grain boundary segregation based on the 0 K properties [35]; a combined experimental-simulation Fe-Cr investigation found good agreement between predicted and observed Cr segregation to Fe grain boundaries [21]. Our model here also assumes very dilute Au concentrations; however, we do not expect these trends to reverse with increasing Au content, as Au is immiscible in Pt at higher fractions (Au-Au bonds are more ener-

getically favorable than Au-Pt bonds). Finally, the 0 K nature of the simulations omits entropic penalties of segregation to the boundary. Lu et al. report Au contents of roughly 25% at grain boundaries in a Pt-10Au (at. %) alloy after 1 hr. at 700 °C, so significant segregation can still occur in Pt-Au alloys at elevated temperatures despite entropic costs. We do not quantify the distribution of Au in this experiment, due to lack of access to a probe-corrected scanning transmission electron microscope. But based on the results of Lu et al. [28], we estimate an Au content of 10-15% at the boundary. For these Au amounts, the preferred facet lies in the low energy region of the $\Sigma 21a[1 \ 1 \ 1]$ -axis tilt grain boundaries. This suggests that segregated Au likely plays a role in stabilizing the faceted grain boundary structures observed experimentally.

3.7. Isotropic curved boundary vs. faceted boundaries

We now take the grain boundary energies calculated in Fig. 4 and use them to estimate lowest energy grain boundary structure between isotropic-curved, pure-Pt-faceted (Fig. 4(d)), and experimentally-observed (Fig. 2(c)) profiles. To estimate the energies of the curved boundary profiles, we assume that they are isotropic, i.e. properties do not vary with angle α). The energy and segregation enthalpy spectrum are taken as the respective averages of the simulated Σ 21a [1 1 1]-axis tilt boundaries.

In order to estimate the energies of the pure-Pt-faceted-profiles (Fig. 4(d)), it is necessary to approximate the size of the pure-Pt-



Fig. 5. Comparison of profile energies in curved and faceted configurations. The experimentally observed grain boundary profiles from Fig. 2(c) are replotted. The profiles are colored to indicate increasing time, rather than the boundary plane normal of each segment. Below these curves, the estimated energies as a function of Au content are depicted. The colored, dashed lines correspond to the isotropic-curved profiles, the colored, dotted lines to the pure-Pt-faceted profiles (Fig. 4(d)), and the colored, solid lines to the experimental/faceted profiles (Fig. 2(c)). The estimated Au content at which the experimental-faceted interfaces become thermodynamically favored over the curved profiles are marked with a black dashed line and written on each plot. The estimated Au ranges in which experimental-faceted structures are energetically favored over both isotropic-curved and pure-Pt-faceted structures are marked with shaded gray region and written at the top of each figure (if predicted to be stable).



Fig. 6. Plots of the GBs looking down the $[1 \ 1 \ 1]$ axis. Each structure is plotted twice. The left plot for each grain boundary colors the atom positions according to centrosymmetry; the right plot colors the atom positions according to the segregation enthalpy of a Au atom to that position. The grain boundary plane normals appear above each pair of structures, and are colored according to the inclination angle α value of that boundary (the color scheme for α is at the top of the figure). The crystal directions in the laboratory frame are plotted below each grain boundary; the directions are marked 'L' and 'R' for the left and right grains, respectively.

faceted grain boundary and the relative length of the two faceting planes according to a method described in Appendix C.

For each grain boundary profile (curved, pure-Pt-faceted, or experimentally-faceted), we calculate the unalloyed energy, along with the segregation spectrum (number of atoms vs. segregation enthalpy), for each segment in the profile. We then calculate the energy of the profiles with increasing fraction of Au occupying the atomic positions at the boundary (see Appendix C). We assume that the Au occupies the grain boundary atomic positions in order of increasing segregation enthalpy, or decreasing favorability (considering all segments of the boundary).

In Fig. 5, we plot our results of these calculations. The profiles from Fig. 2(c) are re-plotted (including the dashed lines for the ideally curved boundary). The color of each profile changes with increasing time. Below each profile, we plot the energy of the curved (dashed line), pure-Pt-faceted (dotted line), and experimentallyfaceted (solid line) configurations of the profile with increasing Au content. The colors of these energy data correspond to the profile used for the calculations. The estimated transitions between the curved and experimentally-faceted configurations are marked with black dashed lines, and the estimated Au content at those transition points are written on each plot. The Au ranges in which the experimental-faceted structures are predicted to be the minimum energy structures are shaded gray. The Au contents at those transitions, if any, are marked at the top of each plot.

From Fig. 5 we can see that the estimated transitions between an isotropic-curved and experimental-faceted configuration occur at relatively low Au fractions in the boundary. Indeed, the estimated transitions generally occur at an Au content that falls within the estimated 10-15% enrichment of Au in the boundary. The results of the simple model suggest that the addition of Au can trigger a transition from a curved to a faceted boundary. In comparison to the pure-Pt-faceted estimations, there is a range of approximately 20–30 at. % Au in which the experimental profiles are thermodynamically predicted to be favorable. This range is higher than the estimated enrichment of Au in the grain boundary and thermodynamic stability is not predicted for several profiles after the ramp up to 800 °C. This ramp appears to briefly force the grain boundary out of equilibrium, until it reaches a (meta)stable state once again. While we cannot exclude a kinetic contribution to why the facets evolved the way they did, there is a sufficient thermodynamic argument for the structure observed.

While making these thermodynamic comparisons to alternate grain boundary profiles, we have not considered the Pt-xAu minimum energy profiles as presented in the gamma plots of Fig. 4(e-f). These profiles are excluded because 1) the minimum energy boundary inclinations already appear (approximately) in the experimental profiles, 2) the experimental observations indicate that not all planes from the gamma plot would contribute to the structure, and 3) by including all predicted gamma plot planes, we would better approximate the isotropic curved profile, thus having lower grain boundary area and lower profile energy.

It is also possible that the grain boundary profiles evolve due to impurity (Au) drag and/or pinning mechanisms that prevent the grain boundary from migrating in the Au-rich regions. While these processes may contribute, we believe that they do not play a dominant role in the formation of the preferred facet structure. The use of the computational modeling reveals that the observed facet structures are thermodynamically favorable configurations because of the Au present; albeit, the experimentally observed inclination angle was slightly different—near-($26 \ \overline{25} \ \overline{1}$)—than the atomistically determined minimum—($1 \ \overline{1} \ 0$)—but the atomic and crystallographic structures of these boundaries are very similar (Figs. 4(c) and 6). Again, we cannot exclude a kinetic contribution, there is

appears to be a sufficient thermodynamic basis for the structure observed.

3.8. Atomic structures of simulated grain boundaries

In Fig. 6, we plot the minimum energy atomic structures of the atomistically simulated grain boundaries in Pt at 0 K. Each grain boundary is plotted looking down the [1 1 1] axis, and each structure is plotted twice: the left plot of each pair has the atom positions colored according to their centrosymmetry parameter (as calculated by LAMMPS per Ref. [36]). The warmer the color (e.g. yellow, red), the less centrosymmetric the surrounding environment of the atom. The right plot of each pair colors the atom positions according to the segregation enthalpy of an Au atom to that atomic position. White atom positions have a segregation enthalpy of zero or a positive value, which is not favorable. Dark atom positions have a negative segregation enthalpy (with the darker the color, the more favorable the segregation to that position). At the top of Fig. 6, the color scheme representing the inclination angle, α , is displayed. This α color scheme is used to shade the boundary plane fundamental zone normal labels above each pair of atomic structures. The crystal directions of each grain in the laboratory frame are identified below each grain boundary.

From Fig. 6, we can see that the grain boundaries have a periodic structure of high and low centrosymmetry. The distribution of segregation enthalpies to atom positions indicates that the segregated Au prefers to cluster at the boundary, with alternating Aurich and Au-depleted regions. This has also been observed in other systems, such as Fe-Cr [35].

We also observe that there is some serration (zig-zagging) in the grain boundaries. Comparing Fig. 4(c) with Fig. 6, we observe that the solute appears to favor boundaries that have some serrations (but not too many or too few). The occurrence of these serrations may explain the discrepancy between the 0 K molecular statics and the experimental observations. From the experiment, preferred facets have near- $(26\ \overline{25}\ \overline{1})$ boundary planes; the simulations indicate that the $(1 \ \overline{1} \ 0)$ boundary plane is the energetic minimum when enriched with 10% Au or more. The energy difference between the $(26\ \overline{25}\ \overline{1})$ and the $(1\ \overline{1}\ 0)$ boundaries, however, is modest. Furthermore, the atomic structures of the these two boundaries are visually very similar, with the same structural features occurring in different amounts. This may suggest that kinetics may be contributing to why the grain boundary prefers the near- $(26\ \overline{25}\ \overline{1})$ plane. In other words, the solute segregated to a near-equilibrium (metastable) facet, which was then unable, kinetically, to achieve the minimum structure.

4. Conclusions

In this work, we have observed a $\Sigma 21a$ grain boundary composed of [1 1 1] symmetric tilt segments in Pt-5Au during *in-situ* annealing. Crystallographic analysis, leaning heavily on the fundamental zone formalism of Patala et al. [8,9], of these segments revealed that they are approximate symmetric equivalents. Comparison of the grain boundary profiles to ideally planar profiles and curved profiles between the triple junctions indicates that the grain boundary appears to favor a curved configuration, implying that the facets serve to minimize the energy of the grain boundary as it approximates this curvature.

We also calculate 0 K interfacial and segregation energies for the $\Sigma 21a$ [1 1 1]-axis tilts. In pure Pt at 0 K, the energies of the boundaries are fairly high (~950 mJ/m²) and not differentiated enough to justify the extra grain boundary area associated with faceting. However, the addition of Au atoms changes the thermodynamic landscape, with decreases in the grain boundary energy γ_{GB} on the order of several hundred mJ/m² or more. These decreases are not homogeneous, with some grain boundaries demonstrating greater thermodynamic sensitivity to the addition of Au than others. The grain boundaries with the greater thermodynamic sensitivity lie near the preferred facet orientation. The agreement between the preferred facet orientation and the molecular statics calculations lead us to conclude that the Au acts to stabilize the preferred orientation.

Comparison of the estimated energies of an isotropic-curved boundary, a pure-Pt-faceted boundary, and the experimental profiles indicates that in an unalloyed condition, the pure-Pt-faceted boundary is favored; with increasing Au content in the boundary, however, there is a range wherein the experimental profiles may become energetically favorable. This indicates that alloying plays an important role in the observed retention of the faceted structure, at least for this alloy for this specific boundary structure. Though other boundary types exist, and could exhibit different responses, this work here has provided a direct experimental observation with modeling to elucidate how solute partitioning can influence the stabilization of facets providing a framework (via the use of the fundamental zone formalism) for other, future studies where similar observations are noted.

The atomic structures of the simulated grain boundaries reveal that the $\Sigma 21a$ [1 1 1]-axis tilt grain boundaries have varying degrees of serration. Comparison of these structures with the alloyed interfacial energies reveals that there appears to be an optimal amount of serration for minimizing the energetic cost of the boundary as solute is segregated to the boundary.

These results reveal a route to the stabilization of grain boundaries against curvature-induced boundary migration, with particular implications for retaining nanocrystalline structures at high temperatures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge NSF-DMR-1709803 for support of this work as well as use of the FEI ThemIS microscope for *in-situ* analysis at the National Center for Electron Microscopy, Molecular Foundry. The Molecular Foundry, Lawrence Berkeley National Laboratory, is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors gratefully recognize the training and feedback on ThemIS operation provided by Peter Ercius and Rohan Dhall. J.L.P. gratefully acknowledges the use of codes written by Eric R. Homer and Srikanth Patala. An insightful discussion with Srikanth Patala is also appreciated.

Appendix A. Σ 21a boundary plane fundamental zone

To develop the $\Sigma 21a$ boundary plane fundamental zone, we repeat a discussion originally presented in Ref. [11]. Fig. A.7 is a visual aid for our explanation of the boundary plane fundamental zone construction. Consider a cube of "infinite" face-centered cubic (FCC) crystal, oriented with the [5 $\overline{4}$ $\overline{1}$] lying on the *x*-axis, the [$\overline{3}$ 2 1] on the *y*-axis, and the [1 1 1] on the *z*-axis. Now picture a sphere cut within this crystal, so that we may rotate the exterior portion while the sphere and its contents remain fixed. If we rotate the cube-minus-sphere 21.8° about the [1 1 1] or *z*-axis, we have achieved a $\Sigma = 21a$ ([1 1 1] 21.8°) coincident site lattice misorientation between the cube-minus-sphere and the sphere. The



Fig. A.7. Brief review of the discussion for the construction of the boundary plane fundamental zone presented in Ref. [11]. (a) represents the Σ 21a ([1 1 1] 21.8°) coincidence site lattice misorientation. The view is down the [1 1 1], and all the possible boundary plane normals lie on the surface of the gray sphere. (b) is a perspective view of the Σ 21a boundary plane normal space. The boundary plane fundamental zone, containing all unique Σ 21a boundary plane normals, is shaded blue. (c) is a stereographic projection of the boundary plane fundamental zone.

surface of the sphere represents all of the possible grain boundary planes between the two crystal orientations. This achievement of the boundary planes via a sphere-within-a-cube is shown in Fig. A.7(a). The $[5\ \overline{4}\ \overline{1}]$ and the $[\overline{3}\ 2\ 1]$ directions in each crystal are marked, along with the rotation between them.

The inherent symmetry of the FCC structure and the the $\Sigma 21a$ misorientation allows us to reduce the total boundary plane spherical surface to a smaller area, known as a *boundary plane fundamental zone*. This fundamental zone (which is for boundary planes, not misorientations) contains all the unique boundary planes for a given misorientation [9]. Fig. A.7(b) contains a perspective view of the sphere which represents the boundary plane space. The plane normals on this sphere are relative to the crystal orientation of the sphere (if comparing to Fig. A.7(a), crystal directions and crystal planes are equivalent for cubic materials). The boundary plane fundamental zone for $\Sigma 21a$ in FCC is shaded blue. All (*h k l*) planes outside this fundamental zone have a symmetric equivalent within this region.

To simplify the representation of fundamental zones, they are often plotted as stereographic projections. The stereographic projection of the particular fundamental zone for this work is plotted in Fig. A.7(c). The vertices/important planes of the fundamental zone are marked with Miller notation, following Fig. A.7(b). We also identify two angles, α and β , that allow us to incline the boundary plane away from (1 1 1). Note that the upper half of the outer arc is a dashed line; this arises because the boundary planes on this section of the arc are symmetric equivalents to those boundary planes on the lower half of the arc. The entirety of the interior of the fundamental zone contains unique boundary planes, only the upper portion of the arc is non-unique [37]. This outer arc contains the $\Sigma 21a$ [1 1 1]-axis tilt boundaries, with the (5 4 1) and (2 3 1) fulfilling the role of [1 1 1] symmetric tilt boundaries. For more details, the reader is referred to the literature [8,9] for a complete explanation of the mathematics underlying the reduction to unique misorientations and boundary planes.

Appendix B. Microstructure changes from 600 °C to 800 °C

Fig. B.8 contains transmission electron micrographs of the faceted grain boundary, showing the changes in local microstructure as the temperature is increased from $600 \,^{\circ}C$ (Fig. B.8(a)) to $800 \,^{\circ}C$ (Fig. B.8(b–c)). The upper triple junction of the faceted grain boundary appears to migrate in response to the migration of neighboring grain boundaries and the elimination of adjacent grains.

Appendix C. Interfacial energy calculations

To calculate the interfacial energies of the alloyed grain boundary segments (Sections 3.6 and 3.7), we employ the following methodology. The interfacial energy γ_{GB} of an arbitrary, doped $\Sigma 21a$ [1 1 1]-axis tilt grain boundary is determined by:

$$\gamma_{GB}(\alpha, \ \tilde{n}) = \gamma_{GB, Pt}(\alpha) + \sum_{\tilde{a}=1}^{\tilde{n}} \left[\Delta \tilde{H}(\alpha, \ \tilde{a}) \right]$$
(C.1)

where	$\gamma_{GB}(\alpha, \tilde{n})$	is the interfacial energy of a boundary with inclination angle α and \tilde{n} atoms per
		area
	$\gamma_{GB, Pt}(\alpha)$	is the interfacial
		energy of the undoped
		boundary
	$\Delta \tilde{H}(\alpha, \tilde{a})$	is the segregation
		enthalpy per unit area
		for an Au atom at the
		ã position

Eq. (C.1) is used to determine the interfacial energies of Fig. 4(c). The values for $\gamma_{CB,Pt}(\alpha)$ are determined by a cubic fit to the $\gamma_{CB,Pt}$ data as a function of α . The list of segregation enthalpies per unit area $\Delta \tilde{H}(\alpha, \tilde{a})$ are determined by linearly interpolating between the boundaries of nearest α . To determine the total energy of each temporal profile with respect to segregation, we first calculate the list of segregation enthalpies for each segment. To do so, we scale the atom sites available by multiplying by the segment area:

$$\Delta H_j(a) = \Delta \tilde{H}_j(\alpha_j, \tilde{a} \cdot A_j) \tag{C.2}$$

is the list of segregation enthalpies for the <i>j</i> th segment
are the atom sites per unit
died
is the segment area

Since we assume that the Au atoms segregate to sites of lowest energy first (followed by higher energy sites thereafter), we must consider all possible atom sites in the boundary profile. Therefore, we make a list of the segregation enthalpies for the entire profile:



Fig. B.8. Transmission electron micrographs of the microstructure near the faceted Σ 21a grain boundary, at 600 °C (a) and 800 °C (b-c). The arrows point to grains in (a) that disappear in (b) and (c).



With this list of segregation enthalpies to the entire profile, we can then calculate the energy of the profile using Eq. (C.4).

$$G(n) = \sum_{j=1}^{J} \left[\gamma_{GB}(\alpha_j) \cdot A_j \right] + \sum_{a=1}^{n} \left[\Delta H_{profile}(a) \right]$$
(C.4)

where	G(n)	is in the energy of the profile
		with n segregated Au atoms

where	R _{perimeter}	is the ratio of the faceted perimeter to the circular
		perimeter
	$p_{\gamma, pure-Pt}$	is the faceted perimeter from
		the pure-Pt-faceted gamma
		plot of Fig. 4(d)
	p_{circle}	is the perimeter of the circle
		that is best fitted to represent
		the pure-Pt-faceted gamma
		plot

We also	estimate th	e ratio	of the	major	facet	length	to	the	total
perimeter in	n the facete	d state	, using	Eq. (C	.7).				

$R_{facets} = \frac{1}{6(l_{l})}$	$\frac{6l_{MAJOR}}{_{AAJOR} + l_{minor})}$	(C.7		
where	R _{facets}	is the fraction of the major facet length over the total perimeter length		
	l _{MAJOR} I _{minor}	is the length of a major facet is the length of a minor facet		

The fraction of atoms in the boundaries is calculated by Eq. (C.5)

$$f_{GB, Au} = \frac{\tilde{n}}{\tilde{n}_{max}} = \frac{n}{\sum_{j=1}^{J} \left[n_{max,j} \right]}$$
(C.5)
where $f_{GB, Au}$ is the fraction of GB atomic
sites occupied by Au
 \tilde{n}_{max} is the total number of GB
atomic sites per unit area for
a single grain boundary
 $\sum_{j=1}^{J} \left[n_{max,j} \right]$ is the total number of GB
atomic sites for a boundary
profile composed of J
segments

To estimate the structure of the pure-Pt-faceted profiles (see Fig. 4(d)), we employ the following methodolgy. First, we determine the ratio ($R_{perimeter}$) of the perimeter of the pure-Pt-faceted profiles to the perimeter of a circle of best fit to the gamma plot, using Eq. (C.6) (see Fig. C.9).

$$R_{perimeter} = \frac{p_{\gamma, pure-Pt}}{p_{circle}}$$
(C.6)

The perimeter (or arc length) of the isotropic curved boundary is estimated using Eq. (C.8).

$curve = r \cdot \alpha$			(C.8
where	p _{curve}	is the perimeter of the isotropic curved boundary	
	r	is the radius of the isotropic	
	α	is the arc angle of the isotropic curved boundary	

Combining Eqs. (C.6), (C.7), and (C.8) together to estimate the free energy of the pure-Pt-faceted profile yields Eq. (C.9).

$$G_{pure-Pt-facets} = R_{facets} p_{curve} (\gamma_{MAJOR} (\chi_{Au}) R_{perimeter} + \gamma_{minor} (\chi_{Au}) (1 - R_{perimeter}))$$
(C.9)

where	$G_{pure-Pt-facets}$	is the free energy of the
	$\gamma_{MAJOR}(\chi_{Au})$	is the interfacial energy of the
		major facets (as a function of
		Au content)
	$\gamma_{minor}(\chi_{Au})$	is the interfacial energy of the
		minor facets (as a function of
		Au content)



Fig. C.9. Schematic detailing the geometric variables that contribute to the estimation of the pure-Pt-faceted profile. The profile is re-drawn from Fig. 4(d).

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