Grain growth and loss of texture during annealing of alloys, and the translation of Earth's inner core

Michael I. Bergman,[1] Daniel J. Lewis,[2] Ingyin Hla Myint,[1] Liam Slivka,[1,3] Shun-ichiro Karato,[3] and Andrew Abreu[2]

[1] The Earth's inner core is seismically anisotropic, with the direction parallel to the rotation axis both fast and more attenuating. There is also increasing evidence that the inner core is asymmetric, with the western hemisphere exhibiting slower direction-averaged P wave velocity, less overall attenuation, and greater elastic anisotropy. It was recently suggested that the hemispherical variations might result from convective translation, whereby enhanced solidification in the western hemisphere leads to a net eastward translation of inner core material, with melting occurring in the east. Annealing accompanies this eastward movement. This study examines experimentally a previously unobserved sequence of grain growth and loss of texture during the annealing of a directionally solidified alloy. The growth of newly nucleated grains results because the original grains that resulted from directional solidification have a high energy associated with intragranular interphase boundaries, and because the minor element has a very low solubility in the primary phase so that a more traditional sequence of coarsening is not possible. This supplies a physical mechanism for the loss of texture that is suggested seismically. **Citation:** Bergman, M. I., D. J. Lewis, I. H. Myint, L. Slivka, S. Karato, and A. Abreu (2010), Grain growth and loss of texture during annealing of alloys, and the translation of Earth's inner core, *Geophys. Res. Lett.*, *37*, L22313, doi:10.1029/2010GL045103.

1. Introduction

[2] One possibility for the hemispherical variations [*Cao and Romanowicz*, 2004; *Niu and Wen*, 2001; *Tanaka and Hamaguchi*, 1997] is that thermal variations in the lower mantle exert long term control over outer core convection, which then get recorded in the solidification texture of the inner core [*Bergman et al.*, 2005; *Aubert et al.*, 2008]. Another possibility, explored here, is that the inner core is translating eastward due to convection [*Alboussiere et al.*, 2010]. As the recently solidified iron alloy crystals move eastward they anneal and undergo grain growth, sufficient to explain the hemispherical differences in seismic P wave velocity and overall attenuation (by means of scattering [*Monnereau et al.*, 2010]). To explain the hemispherical

variation in elastic anisotropy there must also be a loss of texture that accompanies this grain growth, but the mechanism for this loss of texture is not understood. Deformation that could accompany convective translation could result in texture loss. This study suggests a different physical mechanism.

[3] In order to understand the microstructural and textural changes that might occur during the annealing of an iron-rich alloy as it moves eastward across the inner core, we carried out experiments on the annealing of directionally solidified, hexagonal close-packed (hcp) zinc-3 wt pct tin alloys. Annealing is the process during which a material is brought to a high fraction of its melting temperature for some length of time, during which the microstructure can change to reduce high energy microstructural features such as dislocation networks, grain boundaries, and intragranular interphase boundaries.

[4] We use an hcp zinc-rich alloy because the inner core is not pure iron-nickel [*Jephcoat and Olson*, 1987], and because iron under inner core conditions is likely hcp [*Vocadlo et al.*, 2003] (though *Dubrovinsky et al.* [2007] suggest light elements could stabilize a cubic phase). We begin with a directionally solidified microstructure because the inner core may be growing dendritically as a result of directional solidification [*Fearn et al.*, 1981], with hcp dendrites taking on the morphological form of platelets (Figure 1a). The light elements and alloy phase diagram in the core remain uncertain, but oxygen is one likely candidate. Iron oxide exhibits little solubility in iron under inner core conditions [*Sherman*, 1995], which is relevant to this study. Tin has a very low solubility in the zinc-rich phase and, as is likely in the inner core [*Vocadlo*, 2007], the secondary phase (tin-rich in our experiments) is liquid at the annealing temperature.

[5] Aside from the very low solubility of the minor element in the primary phase the exact alloy, or even the crystal structure of the primary phase, is not likely to be important for the changes that we observe that are most relevant for the inner core. The alloy at the annealing temperature is comprised of two phases with mass fractions fixed by the phase diagram. Although the microstructure appears to be reaching a recrystallized, polycrystalline state in the following sequence of micrographs, this is significantly different than a polycrystalline single phase material as the amount of grain boundary in a single phase material is not fixed by having to conserve the mass fraction of secondary phase. This alloy is also substantially different than a two-phase alloy where the secondary phase is distributed as particles in the primary phase. Because of the limited solid solubility and the small volume fraction and morphology of the secondary phase network, the alloy does not lend itself to a classical coarsening process, in which, for instance, dendrite arms

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[1]Physics Department, Bard College at Simon's Rock, Great Barrington, Massachusetts, USA.
[2]Materials Research Center, Rensselaer Polytechnic Institute, Troy, New York, USA.
[3]Department of Geology and Geophysics, Yale University, New Haven, Connecticut, USA.
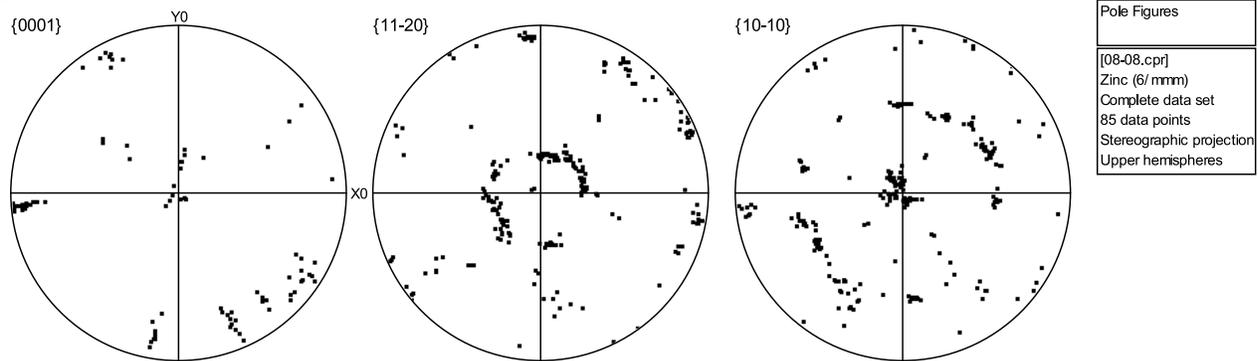
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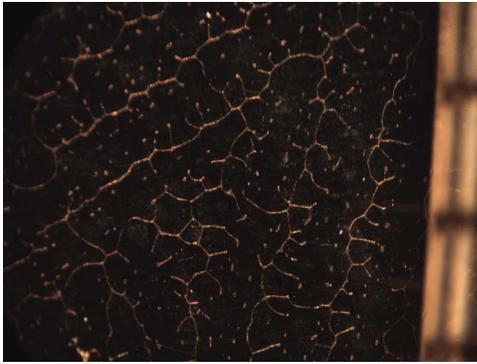
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Figure 1. Directional solidification microstructure and texture. (a) Micrograph of directionally solidified Zn-3 wt pct Sn, transverse to the growth direction. The primary Zn-rich phase is dark, the Sn-rich phase is light. Parallel platelets are part of a single crystal, and a grain boundary lies between two set of parallel platelets. Sidebranching is also evident. Unless a scale is present, all micrograph rulings are 1 mm. (b) A set of pole figures for the sample shown in Figure 1a, relative to the growth direction, showing the growth direction is in the 101'0 direction, with the c-axes primarily transverse to growth. The symmetry of the hcp crystal is such that 101'0 poles near the center also plot on a circle 60 degrees away, and 112'0 poles along a circle at 30 degrees also plot along a circle at 90 degrees.

can coarsen via Ostwald ripening [*Marsh and Glicksman*, 1996], leading to no substantial change in the solidification texture.

2. Experiments

[6] We produced a set of pole figures (Figure 1b), relative to the growth direction, by electron back-scattered diffraction (EBSD) of the directionally solidified alloy shown in Figure 1a. Although the sample contains only tens of coarse grains, the pole figures are consistent with the solidification texture common to hcp alloys, where the c-axes lie transverse to the growth direction [*Bergman*, 1997]. We then annealed a 1 cm thick section from near mid-height of a 4.45 cm diameter, approximately 19.0 cm tall, directionally solidified ingot by placing it in a graphite crucible, and reheating it to 397 deg C, which is 0.97 of the homologous temperature of pure Zn. We annealed each section for a time ranging between one hour and ten days. At the end of the annealing we removed the section and quenched it in water. We then repolished the section to examine optically the annealed microstructure, in particular, observations of the grain and sub-grain morphology. We then used EBSD to determine crystalline orientation and produce pole figures. Pole figure creation was completed using a uniform density

of points in the region of interest. The number of points used to generate the pole figure is included in Figure 1b. We estimate an uncertainty of no more than 5 degrees in the measured orientation of the sample surface relative to the specimen growth direction. These uncertainties arise due to the metallographic preparation, sample mounting in the SEM, and mechanical stage alignments. In some cases automated EBSD measurements were completed to increase the amount of data collected and produce grain orientation maps.

[7] After four hours of annealing the dendritic sidebranches within an individual platelet have coalesced. As the individual sidebranches disappear the Sn-rich secondary phase breaks down into detached pockets that often appear as concave diamond shapes in 2-D sections. Since there is very little misorientation on opposing sides of the Sn-rich phase separating secondary dendrite arms (we estimate less than two degrees based on EBSD measurements), and there is a lowering of total interphase boundary area when the individual secondary arms coalesce [*Martin et al.*, 1997], there is a decrease in free energy due to interphase interfaces as the microstructure evolves.

[8] We hypothesize that self-diffusional processes in the solid Zn-rich matrix are the main means that aid in the redistribution of the Sn-rich phase, resulting in the reduction of the interphase boundary area [*Burke and Turnbull*, 1952].
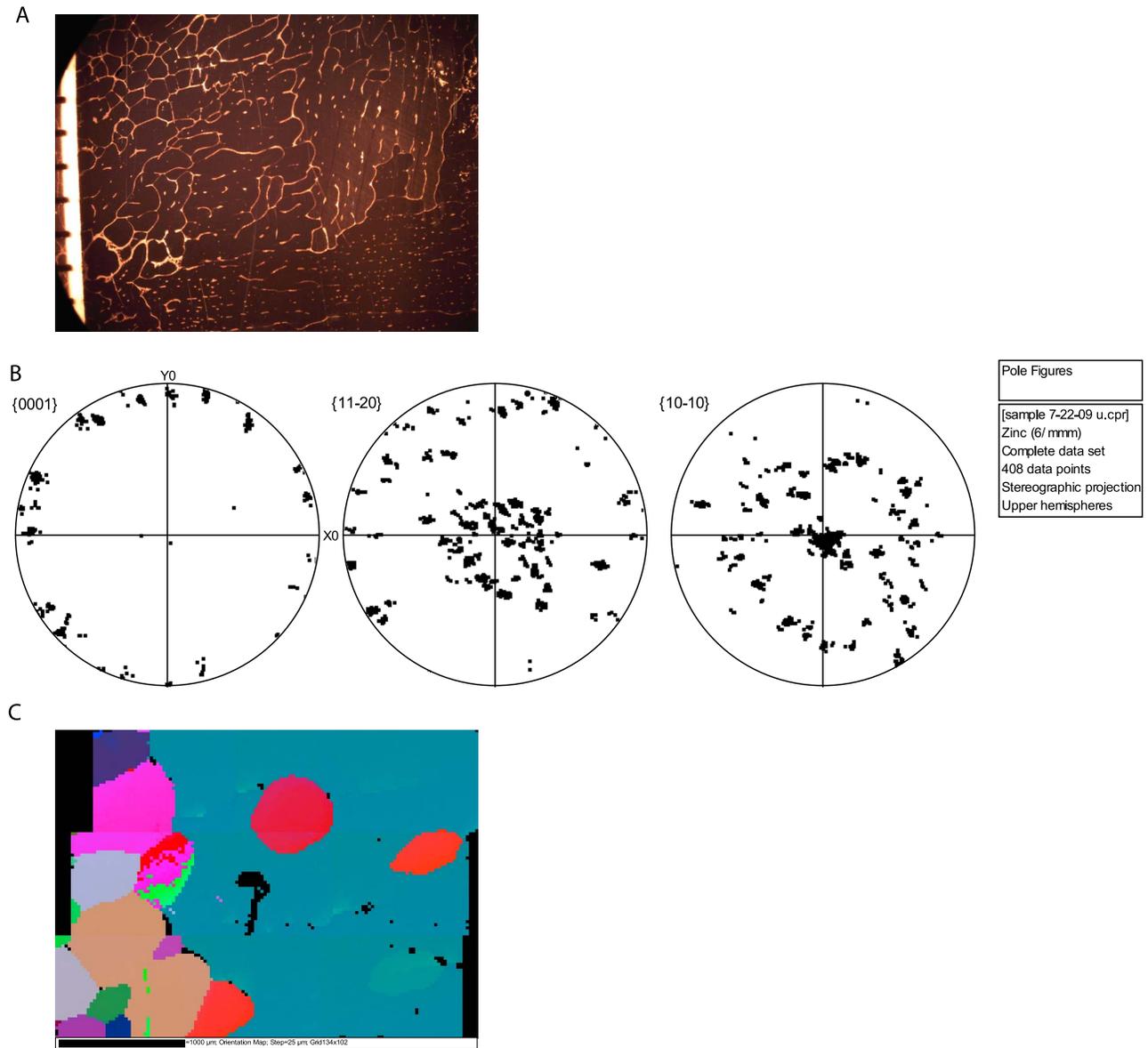
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Figure 2. Annealing microstructure and texture. (a) Micrograph of directionally solidified Zn-3 wt pct Sn, then annealed for 30 hours, transverse to the original growth direction. The platelet boundaries are breaking up, and some of the original, large grains are showing new, smaller grains growing. (b) A set of pole figures for the sample shown in Figure 2a, relative to the original growth direction. The texture is essentially the same as in Figure 1b, though somewhat more random. (c) A large scale orientation map for the sample shown in Figure 2a, showing new, small grains with an orientation unrelated to the original, large grain, as well as a region to the left that is now all polygonal grains with a random texture.

This self-diffusion mechanism should be contrasted to a more traditional coarsening analysis where the diffusion of solute in the matrix controls the microstructure development. It is likely that solute diffusion in the Zn matrix does not play a critical role in the morphology change due to the insignificant solubility of Sn in Zn. Pole figures for the section annealed for four hours show little change in texture from the un-annealed, directionally solidified alloy, and is consistent with the diffusion analysis.

[9] After 30 hours evidence of platelet boundary breakup is observed, though the original, large grains are mostly still intact. Figure 2a shows a lower magnification image where it is possible to identify grain boundaries as well as prior-

platelet boundaries. In an instability akin to a Rayleigh, or capillary, instability [*Chandrasekhar*, 1961] the platelet boundaries become segmented so that individual platelets coalesce and in the 2D section individual secondary phase "particles" detach and decorate the prior platelet boundary. Figure 2b is the corresponding set of pole figures, which still shows little fundamental change in texture.

[10] However, after 30 hours of annealing some regions are beginning to show new grains with polygonal morphologies. See, for example, the grains in the upper left corner of Figure 2a. Using an automated EBSD stage we made a large scale orientation map (Figure 2c) of the texture of a selected region of this sample, showing that a new, small grain has
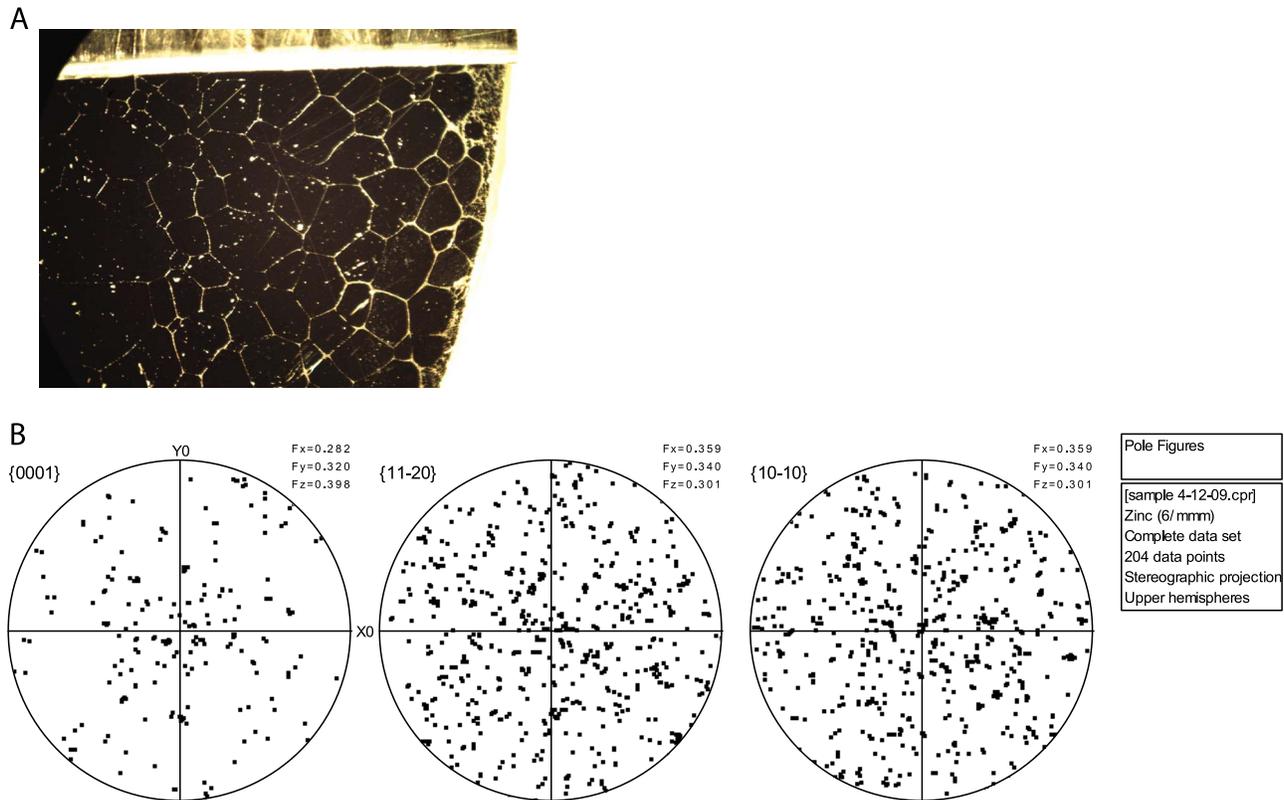
Figure 3. Grain growth. (a) Micrograph of a section of directionally solidified Zn-3 wt pct Sn, then annealed for 120 hours, transverse to the original growth direction. The original, large grains comprised of parallel platelets have been eaten up by newly nucleated grains that have grown as polygons. (b) A set of pole figures for the sample shown in Figure 3a, relative to the original growth direction. The texture is now random, as a result of grain growth from randomly oriented, newly nucleated grains.

an orientation that is unrelated to the orientation of the original, large grains comprised of platelets. Given the small size and unrelated orientation of these new grains we believe they are the result of nucleation of new Zn-rich crystals with random orientations.

[11] Indeed, by 120 hours the entire surface exhibits a polygonal structure (Figure 3a), which is characteristic of recrystallization and grain growth [*Humphreys and Hatherly*, 1996], and is supported by the corresponding pole figures, Figure 3b, that now show a random texture. At this time the growing grains are larger than the width of the original platelets, but somewhat paradoxically, smaller than the original grains comprised of platelets. At 240 hours the polygons continue to grow, though we did not carry out even longer experiments in an attempt to find the growth exponent.

[12] Dendrites and platelets during directional solidification are kinematically stable structures, but they are not necessarily thermodynamically stable, so that Ostwald ripening typically occurs during the annealing of alloys [*Marsh and Glicksman*, 1996]. However, the transformations that occur during the annealing of an alloy with very limited solid solubility have not been previously investigated. We expect that new grain nucleation events replace microstructural features that have greater potential energy. We recognize two sources of stored energy in the original grains comprised of platelets that may drive such a process: 1) stresses and or mechanically induced defects from solidification processing and 2) the energy associated with the interphase boundary

area. The authors would not expect the energy associated with deformation during solidification and subsequent annealing to be large, though we did not attempt to measure dislocation densities. On the other hand, Figures 1a, 2a, and 3a suggest that the energy associated with intragranular interphase boundaries within the original, large grains could be significant, thus allowing the new, small grains to grow while pushing all the secondary phase to the grain boundaries. This rearrangement of the secondary phase results in a random texture once the newly nucleated grains have time to grow.

[13] Figure 4 supports this hypothesis on the change in grain morphology and resulting texture. Figure 4a is a high magnification micrograph showing two new, small Zn-rich grains without any pockets of the secondary Sn-rich phase, surrounded by the original, large grain with many small pockets of the secondary phase. This is perhaps reminiscent of recrystallization and the growth of a relatively defect-free, small, new grain into a heavily deformed, larger grain with a high dislocation density.

[14] Figure 4b is a plot of the normalized interphase boundary for the isothermally annealed sections at different annealing times, produced by carrying out quantitative image analysis on a series of images taken at different annealing times. In this analysis we measured the perimeter of the interphase boundary, and normalized it to the total area inspected. This metric, the interphase perimeter per unit area, supports the hypothesis that the microstructural evolution in these directionally solidified materials is a
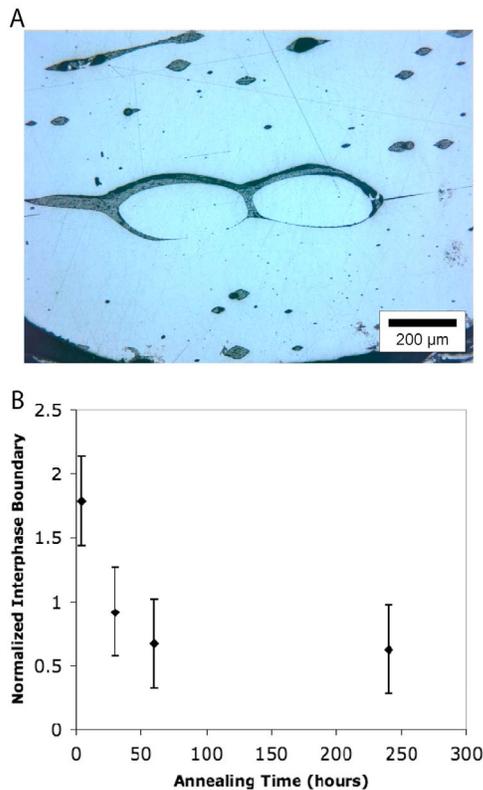
Figure 4. Reduction in interphase boundary energy. (a) A high magnification micrograph taken under a stereoscope of a section of directionally solidified Zn-3 wt pct Sn, then annealed for 30 hours, transverse to the original growth direction (as for Figure 2a). The primary Zn-rich phase is light, the Sn-rich phase is dark. The micrograph shows two new, small Zn-rich grains without any pockets of the secondary Sn-rich phase, unlike the surrounding old, large grain. (b) A plot of the normalized interphase boundary for isothermally annealed sections at different annealing times.

relaxation process even though the crystal misorientation distribution becomes more random as new grains appear with orientations different than the parent group of platelets. The results presented in Figure 4b represents the means of five fields of view and the error bars are plus and minus one standard deviation for the 30 hour anneal time. This was the largest standard deviation.

3. Discussion

[15] The following sequence of morphological steps occurs during annealing of hcp-rich, directionally solidified alloys that exhibit low solubility: 1) side arm coalescence, 2) platelet boundary instability, 3) nucleation of inclusion-free grains, and 4) grain growth. The details of some of these steps are still uncertain, e.g., the platelet boundary instability, and the nucleation of new grains, though ultimately the microstructure is relaxing by reducing the total amount of interphase boundary. To gain a more detailed understanding of these steps additional experiments and numerical studies are necessary. Ultimately the polygonized microstructure has no residual texture associated with the directional solidification process. We hypothesize that the

new grains formed during morphological step 3 are the nucleation events that lead to a randomized texture.

[16] As the directionally solidified iron alloy in the inner core moves eastward as a result of enhanced solidification in the westward hemisphere [*Alboussiere et al.*, 2010; *Monnereau et al.*, 2010], it is annealing. This results in grain growth, though a classical model may not apply because the intergranular phase volume is fixed. Moreover, the grains that grow are not likely to be the large, original, directionally solidified grains that are thermodynamically unstable due to a high internal interphase boundary energy. Rather, the grains that grow are likely to be newly nucleated grains that are relatively free of the secondary phase, pushing the secondary phase to the grain boundaries. These newly nucleated, growing grains have a random texture, as seen in Figures 2c and 3b.

[17] This suggests that if one of the light elements in the core has low solubility in iron [*Sherman*, 1995], and if the inner core is convectively translating [*Alboussiere et al.*, 2010], then the inner core texture should weaken from west to east, with length of annealing time after solidification. It is difficult to estimate precisely the time for the texture to weaken because of the uncertainty regarding the grain growth exponent. In pure materials, theory predicts the grain size $R = (M\gamma t)^{1/2}$, where M is the grain boundary mobility, γ is the surface energy, and t is time [*Humphreys and Hatherly*, 1996]. Experimentally, the exponent is usually less than $1/2$. In alloys, the theory is less well-developed, but the exponent is typically $1/3$ to $1/4$, both in theory and measured experimentally.

[18] The mobility in metallic alloys is strongly dependent on the metal, temperature, alloy concentration, and boundary orientation (and perhaps pressure!), with laboratory values typically in the range 10^{-3}–10^{-11} m^4/J-s, while the surface energy is of the order of .1 J/m^2 [*Humphreys and Hatherly*, 1996]. Choosing intermediate values $M\gamma = 10^{-8}$ m^2/s, the growth exponent to 1/3, and the time t = 50 million years (about half the time estimated for complete inner core translation), yields R = 500 m. This is similar in size to the estimated size of the original dendritic grains [*Bergman*, 1998], so that perhaps half of the original, textured grains will have been eaten up by new, randomly oriented grains in about half the time for inner core material to traverse across the inner core. Obviously this is an extremely crude calculation with a wide uncertainty, but it does suggest that texture loss in the inner core by the mechanism observed in these experiments falls within a range of plausible values. It thus seems possible that annealing during translation could help explain east–west asymmetry in elastic anisotropy. Depth dependence in the more anisotropic western hemisphere remains an enigma, but could be due to a geometrical effect associated with solidification texturing [*Bergman*, 1997].

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A. Abreu and D. J. Lewis, Materials Research Center, Rensselaer Polytechnic Institute, 110 Eighth St., Troy, NY 12180, USA.

M. I. Bergman, I. H. Myint, and L. Slivka, Physics Department, Bard College at Simon's Rock, 84 Alford Rd., Great Barrington, MA 01230, USA. (bergman@simons-rock.edu)

S. Karato, Department of Geology and Geophysics, Yale University, PO Box 208109E, New Haven, CT 06520, USA.