Crystallographic and compositional contributions to the breakdown of the $\text{GdNi}_{1-x}\text{Co}_x$ solid solution

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Abstract

The GdNi-GdCo pseudo-binary system, $\text{GdNi}_{1-x}\text{Co}_x$, has been investigated by scanning electron microscopy (SEM). While x-ray powder diffraction analysis indicates the existence of the GdNi-type phase in samples up to $x=0.50$, SEM investigation of the $x=0.50$ sample reveals a two-phase microstructure consisting of the GdNi (1:1) phase and an new $\text{Gd}_3(\text{Ni},\text{Co})_2$ (3:2) phase. Energy dispersive x-ray spectroscopy (EDS) of the 1:1 phase in the $x=0.50$ sample indicates a composition near $\text{GdNi}_{0.60}\text{Co}_{0.40}$ which is assumed to be the upper limit of the solid solution. The persistence of ~ 5 vol.% of a $\text{Gd}(\text{Ni},\text{Co})_2$ -type (1:2) secondary phase, fine features penetrating entire grains, and slight Ni,Co composition changes are observed in samples from $x=0.00$ to 0.30. EDS analyses of these 1:2 regions indicate a sharp increase in Co with increasing x , while the matrix remains at the nominal composition despite variations suggested from backscattered electron (BSE) imaging. Electron backscattered diffraction analysis points to significant texturing with large similarly oriented grains; the coupons have an overwhelming tendency to grow in the [010] direction in columnar grains roughly $50\mu\text{m}$ wide and hundreds of microns long. BSE images of $x=0.30$ sectioned along the long direction (yz) of the grains exhibit contrast variations reminiscent of “tiger stripes” while those of surfaces cut perpendicular to the long direction(xy) exhibit long thin features (“stitches”) surrounded by darker dendritic regions. Orientation Imaging Microscopy (OIM) of the stitches reveals small rotations of roughly 40° from one side of the stitch to the other, fitting with a mirror twin on the (110) plane. The formation of these twins is assumed to relieve stress caused by the incompatibility of Co in the GdNi matrix and the directional solidification during arc melting.

Keywords: Electron Microscopy, Magnetoelastic Materials, Gadolinium, EBSD, WDS, Rare Earth

1. Introduction

Lanthanide-transition metal alloys continue to attract a great deal of attention by the scientific community as many of these alloys exhibit physical behaviors that are interesting to both basic and applied science. For example, the magnetocaloric effect which is observed as a reversible entropy or temperature change in response to a varying magnetic field was documented as early as 1918.[1, 2] Following the work of Brown[3], who demonstrated the feasibility of magnetic cooling near room temperature, the discovery of the

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Figure 1. Crystal structure of Gd(Ni,Co), the blue box is the unit cell, Gd-Gd and (Ni,Co)-(Ni,Co) bonds are present to show the layered nature of the material.

”giant” magnetocaloric effect (GMCE) in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [4] using high purity Gd[5] accelerated the prototyping of magnetic refrigeration systems containing these and related materials.[6] The renewed interest in calorics has also encouraged the discovery of other material systems which exhibit this phenomenon.[7, 8] Other materials in this family which couple large magnetostriction and high sensitivity can find applications as so-called magneto-elastic stress sensors and are generally referred to as magnetoelastic materials.[9] Indeed, a number of systems have been studied including the lanthanide-nickel (R-Ni) alloys, first examined independently by Abrahams[10], Walline[11], and Dwight.[12] GdNi, like many other light lanthanide R-Ni alloys, is orthorhombic and orders in the CrB-type structure (space group Cmcm)[11, 13, 14, 15] depicted in Figure 1; its Curie temperature (T_C) is the highest among R-Ni alloys, and it exhibits a large spin-only magnetic moment[10]. GdNi, along with GdCu_2 , has also been shown to exhibit an anomalous thermal expansion below its T_C .[16] While both GdNi_2 and GdCo_2 exhibit substantial magnetocaloric effect [17], the GdNi (1:1) compound has both appreciable magnetocaloric effect and has been found to display non-trivial magnetoelastic coupling and a large anisotropic magnetostriction.[18]

Interestingly, there exists a relationship between the effects of magnetoelastic behavior in GdNi and the effects of Ni-Co substitution in the $\text{GdNi}_{1-x}\text{Co}_x$ system ($x \leq 0.30$).[19] This correlation was noted in lattice parameters calculated from Rietveld analysis of X-ray powder diffraction (XRD) and magnetic measurements of selected compositions in this alloy system. The XRD patterns of the samples indicate systematic changes in lattice parameters between $x=0.00$ and $x=0.30$ compositions (corresponding to the shifts in Bragg peaks visible in Figure 2). Further, comparison between the as-cast and annealed samples reveals a distinct sharpening in many of the Bragg peaks attributable to improved chemical homogeneity upon annealing.

Figure 2. X-ray Diffraction Patterns for the range of compositions and heat treatments (AC: as-cast; AN: annealed 800°C 7 days; AL: annealed 700°C 18 days). Significant peak sharpening for $x=0.05$ through $x=0.30$ occurred during annealing. Notice the peak shift with composition is most apparent in the AN or AL samples. Peaks in $x=0.00$ to $x=0.30$ all belong to the 1:1-type phase. Extra peaks begin to appear in $x=0.50$ suggesting a second phase and neither phases are present in $x=1.00$. Selective reproduction of patterns marked with * from Ref. [19].

The appearance of additional Bragg peaks in the XRD pattern of $x=0.50$ suggests a secondary phase formation and an end to the solid solution. The $x=1.00$ sample exhibits a completely different diffraction pattern. As the solid solution was the main focus of the previous investigation[19] these additional peaks in $x=0.50$ and $x=1.00$ XRD patterns were not identified but will be investigated here. Similarities between the trend in lattice parameters with varying composition and the magnetostriction of GdNi at 60 K suggest a difference in magnetic Gd-Ni and Gd-Co interactions as an impetus for the anomalous lattice parameters change and, ultimately, structural instability. Namely, the influence of Co on the GdNi structure is similar to the influence of the applied magnetic field.[20] This link between composition and magnetostriction can be potentially useful to enhance, or to specially tailor the effect for application in magnetoelastic sensors, actuators, or transducers.

It is well known that the sensitivity of XRD analyses to detect impurity phases is limited to a few volume

percent, but for Gd-based systems investigated by Cu K_{α} radiation, whose energy is near the L-absorption edge of Gd, the limits of detection can be much worse.[21] Further, secondary phases in an extraordinarily responsive specimen like $Gd_5(Si,Ge)_4$ can have significant effects on bulk magnetic behavior; small inclusions of $Gd_5(Si,Ge)_3$ actually seed the paramagnetic to ferromagnetic transition in the $Gd_5(Si,Ge)_4$ matrix, promoting the formation of the low-volume ferromagnetic phase in the bulk due to stress concentrated in a narrow interfacial region between the platelet-like inclusions and the matrix.[22]

For the $GdNi_{1-x}Co_x$ system, differences observed in the density of states near the Fermi level when Ni is replaced by Co have been suggested as the main reason for the termination of the solid solution [19], and previous studies [20] have answered some questions about the nature of the magnetism and its effect on the crystal structure of GdNi. However, the behavior observed when shifting the composition toward GdCo raises many other questions including but not limited to: how the Co concentration affects the microstructure and local crystal structure; what impact, if any, does annealing have on the microstructure and phase purity; and exactly how much Co can be accommodated in the parent GdNi lattice. In this study these questions have been answered using electron microscopy, associated spectroscopy techniques, and closer inspection of the previously available data.

2. Experimental

High purity Gadolinium was prepared by the Materials Preparation Center of Ames Laboratory. Major impurities include: O (342 ppm wt.), C (153 ppm wt.), N (370 ppm wt.), Fe (20 ppm wt.), Cu (9.3 ppm wt.), La (1.9 ppm wt.), Ce (49 ppm wt.), Pr (3.9 ppm wt.), Tb (3.6 ppm wt.), Yb (<20 ppm wt.), and W (1.6 ppm wt.) for an overall purity of (99.86 at.% with respect to all elements). Nickel and Cobalt were both purchased commercially (>99.9 at.% with respect to all elements). In total, eight compositions were prepared and investigated ($x=0.00, 0.05, 0.10, 0.15, 0.20, 0.30, 0.50$, and 1.00) in the rather sparsely populated composition space of the Gd-Ni-Co ternary phase diagram available (Figure 3).

Each alloy was arc melted in ≤ 10 -g buttons, flipped and re-melted multiple times to ensure homogeneity. Typical weight loss during melting was less than 0.1 wt%. The samples were sealed in quartz tubes, filled with He at roughly 0.3 bar and heat treated at various temperatures and lengths to reach equilibrium. Analyses were performed for each of these three states: as-cast (AC), annealed at 800°C for 7 days (AN), and annealed at 700°C for 18 days (AL). Powder X-ray Diffraction (XRD) was carried out using a PANalytical X'Pert diffractometer employing Cu K_{α} radiation. Samples of each composition were prepared for microscopy analysis via traditional methods (i.e. grinding and polishing) with a final step employing a 0.25 μm diamond

Figure 3. Limited available phase information in the Gd-Ni-Co system showing compositions of samples (red dots) being investigated following the formula $\text{GdNi}_{1-x}\text{Co}_x$. [23]

suspension. Electron microscopy characterization was performed using a JEOL 5910 scanning electron microscope (SEM) with a Noran Vantage energy dispersive x-ray spectroscopy (EDS) system and solid-state backscattered electron (BSE) detector. Orientation imaging microscopy (OIM) was performed using an Amray 1845 Field Emission SEM equipped with an EDAX electron backscattered diffraction (EBSD) detector and TSL OIM analysis software. Wavelength dispersive x-ray spectroscopy (WDS) spectra were measured using a JEOL JXA-8200 microprobe at 15kV 25nA probe diameter of $8\mu\text{m}$. The Nickel K_α (measured at 115.4 nm), Cobalt K_α (124.6 nm), and Gadolinium L (142.4 nm) were all measured on LIF crystal for diffraction. Peaks were measured for 15 seconds while high and low backgrounds were measured for 5 seconds approximately 5mm above and below the peak positions. For clarity of further analyses both carbon and oxygen signals ($\leq 7\text{at.}\%$ combined) were removed from EDS and WDS measured compositions as surface oxidation and contamination occurs rapidly.

3. Results and Discussion

SEM images of as-cast samples ($x=0.00$, 0.30 , 0.50 , and 1.00) can be seen in Figure 4. A two-phase system appears at $x=0.50$ indicating the definite cessation of the solid solution of the GdNi based CrB crystal structure (“1:1”). The microstructures of $x=0.00$ and 0.30 samples both exhibit large matrix grains with small amounts of secondary phase regions (dark spots in Figure 4(a and b)) determined by EDS to match compositionally to the MgCu_2 -prototype cubic Laves phase $\text{Gd}(\text{Ni},\text{Co})_2$ (“1:2”). Though the 1:2-type phase is present in the SEM images (Figure 4) the small volume concentration ($< 5 \text{ vol.}\%$) prevented detection via XRD (absence in Figure 2), which appeared to be single phase. More interesting however, are the more subtle contrast variations present in BSE images of both $x=0.00$ and $x=0.30$. These features permeate entire matrix grains and appear to encompass a large fraction of the structure. The XRD results indicate that the observed contrast is not due to the presence of two different crystal structures, suggesting a chemical segregation in the same CrB-prototype structure (e.g. spinodal decomposition). Slight variations in EDS and WDS analysis across these features showed no consistent change in composition from one feature to another, likely due to their small size and homogeneous distribution. The $x=0.50$ sample exhibits a two-phase microstructure consisting of the 1:1-type (the darker phase) and a phase fitting compositionally between $\text{Gd}_3(\text{Ni},\text{Co})_2$ and $\text{Gd}_4(\text{NiCo})_3$ (the lighter phase). WDS analysis of these phases can be seen in Table 1. This is consistent with the rejection of Co from the 1:1 phase discussed previously and indeed the composition of the 1:1 phase in $x=0.50$ is roughly 23 at.% Co and 27 at.% Ni. This segregation may indicate an upper limit to the solid solution of Co in the 1:1 phase at $x=0.45$. The $x=1.00$ (GdCo) sample has a

Figure 4. SEM images captured in backscattered electron detector mode for as-cast samples (a) $x=0.00$, (b) $x=0.30$, (c) $x=0.50$ (d) $x=1.00$. (a and b) gray spots are $\text{Gd}(\text{Ni},\text{Co})_2$ -type secondary phases, while the other features are of unknown origin with no discernible composition difference from the matrix. (c and d) breakdown of the solid solution is evident and a completely different microstructure is observed. (c) light regions are $\text{Gd}_3(\text{Ni},\text{Co})_2$ -type or $\text{Gd}_4(\text{Ni},\text{Co})_3$ -type phase, dark regions $\text{Gd}(\text{Ni},\text{Co})$ -type phase. (d) light phase is Gd_2Co , matrix phase is approximately Gd_4Co_3 while the dark dendrites are $\text{Gd}(\text{Co})_2$

dendritic microstructure where the dendrites match the 1:2 phase and the matrix phase is near Gd_4Co_3 , both of which have been reported in the Gd-Co system. Also of note is a light phase in Figure 4(d) with a composition near Gd_2Co ; this phase is not present in any of the Gd-Co phase diagrams reported in literature.

Upon annealing, “tiger stripes” of lighter and darker regions were observed for $x=0.00$, 0.15 and 0.30 (Figure 5). This is likely due to the coarsening of the features observed in the as-cast samples. Further, it is noted that the 1:2 phase regions become both larger and more homogeneous (in the case of $x=0.00$) after annealing due to uptake of Ni/Co. Both the $x=0.50$ and 1.00 samples melted upon annealing, which is consistent with the presence of low-temperature eutectics in both Gd-Ni and Gd-Co binary phase diagrams; therefore only the data from as-cast samples were considered for these compositions.

The microstructures of most interest are of those samples near a composition of $x=0.30$ as this is the

Figure 5. SEM images captured in backscattered electron detector mode for annealed samples (a) $x=0.00$, (b) $x=0.15$, (c) $x=0.30$ (a-c) EDS indicates gray spots are $\text{Gd}(\text{Ni},\text{Co})_2$ -type secondary phases, while stripes are either too small or too close in composition to determine any difference through EDS.

Figure 6. $\text{GdNi}_{0.7}\text{Co}_{0.3}$ as-cast (a), annealed 800°C for 7 days (b), and annealed 700°C for 18 days (c). Note the change in the features from slight fluctuations (a) to regular stripes (c), with (b) exhibiting the stripes to a lesser degree but with very large secondary phase regions.

region where samples begin to show an anomalous magnetic behavior wherein T_C decreases with increasing $x(\text{Co})$. [19] As-cast and annealed $x=0.30$ samples exhibit contrasting regions in BSE images indicating slight fluctuations in composition (Figures 4,5,6). Notably, the degree of variations in BSE mode images increases with annealing for long periods, and the 1:2-type phase regions appear to grow in size (Figure 6). EDS analysis of the 1:2-type regions indicate an increase in Co composition with annealing (Figure 7).

Despite the presence of the 1:2 phase in all samples up to $x=0.3$ the composition of the matrix phase was relatively consistent and very near to the nominal composition (Table 1). The variations noted in Nickel and Cobalt may be a result of sampling the fine features rather than actual variations, while the Gadolinium composition remained relatively steady.

Since SEM/EDS and WDS were inconclusive in determining whether the nature of the tiger stripes is related to compositional variation, OIM was used to determine whether local crystallographic variations existed which could account for the observed contrast (Figure 8). The grains present are very large and elongated, with grains $30\text{--}60\text{ }\mu\text{m}$ wide and 100's of microns long. The out of plane orientation for each pixel in Figure 8(a) corresponds to the legend in Figure 8(c) and was compiled and presented as a surface plot of

Figure 7. Averaged EDS point scans of the 1:2-type phase regions in $x=0.30$ AC, AN, and AL samples. Slight, but significant increase in Co composition from AC to both AN and AL. Possibly due to larger sampling regions and less overlapping interaction volume with the matrix.

Table 1. WDS data for samples $x=0.00, 0.15, 0.30, 0.50$ and 1.00 averaged for all available heat treatments. Note the composition of the second phase ($\text{Gd}_3\text{Ni}_2\text{Co}_4$ in $x=0.15$). Rows marked with * indicates data presented in [19], † denotes new data.

$x(\text{Co})_{\text{nom.}}$	Phase	Averaged Composition (at.%, O-corrected)			$x(\text{Co})_{\text{meas.}}$
		Ni	Co	Gd	
0.00	(1:1)	49.62 ± 0.26	0.00 ± 0.00	50.38 ± 0.26	0.00 ± 0.00 *
0.00	(1:2)	67.23 ± 0.24	0.00 ± 0.00	32.77 ± 0.24	†
0.15	(1:1)	42.49 ± 0.40	7.22 ± 0.44	50.29 ± 0.47	0.15 ± 0.01 *
0.15	(1:2)	22.13 ± 0.19	44.08 ± 0.03	33.79 ± 0.19	†
0.30	(1:1)	35.25 ± 0.84	14.73 ± 0.83	50.02 ± 0.22	0.29 ± 0.02 *
0.30	(1:2)	12.26 ± 0.47	54.80 ± 0.40	34.47 ± 0.05	†
0.50	(1:1)	27.97 ± 1.52	22.69 ± 1.56	49.34 ± 0.23	0.45 ± 0.03 †
0.50	(3:2/4:3)	16.03 ± 0.81	25.14 ± 0.70	58.83 ± 0.38	†
1.00	(11:9)	0.00 ± 0.00	45.79 ± 0.21	54.21 ± 0.21	†
1.00	(2:1)	0.00 ± 0.00	36.23 ± 1.98	63.77 ± 1.98	†
1.00	(1:2)	0.00 ± 0.00	67.25 ± 0.19	32.75 ± 0.19	†

Figure 8. (a) OIM generated Inverse Pole Figure showing grain orientation (legend present in (c)), large, namely very long grains oriented near the [001] direction out of the plane of the image. While slight rotations are observed from one grain to the next, most are oriented with the [010] near the long direction indicating a highly textured microstructure. (b) Surface plot of individual pixel orientations showing texturing out of the plane of the page.

texture in Figure 8(b). The long direction of the grains was found to be the [010] suggesting a preferential solidification direction. Relatively small misalignments are observed between these grains; in the image shown only a single small grain at the top exhibits a large rotation from the neighboring grains ($>60^\circ$).

The long dimension of the grains aligned with the vertical direction of the arc melted button, typically the dominant thermal gradient during solidification, similar to what was observed in $\text{Gd}_{11}\text{Ni}_4\text{In}_9$. [24] All initial samples (i.e. those containing tiger stripes) were cut parallel to that direction (called the “yz” direction). One sample in the as cast state was sectioned on a face perpendicular to the previous samples (denoted “xy”) revealing a completely different pattern of light and dark regions. In this case the matrix appeared light with darker dendrite-like regions with very fine, straight lines in the middle which are not continuous but instead broken up like stitches. These “stitches” are present along the axis of the dendrites and can be seen in Figure 9a. The BSE images indicate a slight but noticeable difference in composition from matrix to “dendrite” to 1:2 phase.

The EDS results (Figure 10) indicate a slight but noticeable shift in composition between these areas.

Figure 9. BSE compo-mode images of $x=0.30$ (a) as-cast, and (b) annealed. Note the change in the darker dendrites from the as-cast to the annealed specimen. As with other images, the dark spots are the 1:2-phase while the gray matrix and the darker gray dendrites remain near the 1:1 composition with variations in Co and Ni.

EDS point analyses of the stitches indicates a lower Co concentration while the dendrites directly surrounding them contain more Co than the matrix area, which remains near the nominal composition. Even considering the large variations in the data there is still clear separation in composition between the stitches and the dendrites suggesting that the stitch is a favorable state, either compositionally or structurally. If these stitches are as thin as they appear ($\sim 200\text{nm}$) a large majority of the x-rays considered as coming from the stitch are actually produced by the region immediately surrounding the stitch. However, an EDS line scan across a stitch reveals a reduction in Co and a simultaneous increase in Ni while the Gd signal remains the same; the EDS profile can be seen in Figure 11 next to an image of the region of interest. This scan was performed across a stitch in the region identified as being the matrix between darker contrast dendrites. The results corroborate what was seen in the point analyses, namely, the stitch appears to reject Co to the surrounding areas with the intensity profile suggesting a kinetic process (e.g. diffusion) responsible.

OIM was performed to determine grain structure and orientation on the as cast $x=0.30$ “ xy ” sample. The difference in microstructure from the previous “ yz ” to this orientation is notable. Small needle-like grains are intermixed with larger ones, which would seem to extend through the material (Figure 12). Again, the out of plane orientation for each pixel in Figure 12(a) corresponds to the legend in Figure 12(c) and was compiled and presented as a surface plot of texture in Figure 12(b). The majority of the grains are oriented within a few degrees of the $[010]$ direction out of plane which is in excellent agreement with OIM of the “ yz ” orientation. The small needle-like grains (indicated by black lines in Figure 12) have an angular relationship of approximately 37° with only one of their neighbors each, indicating a crystallographic relationship. This

Figure 10. Averaged EDS point analyses, notice Ni-Co tradeoff between stitch and dendrites while matrix remains near nominal. Error bars are one standard deviation of data set.

Figure 11. EDS linescan across a linear feature in $\text{GdNi}_{0.7}\text{Co}_{0.3}$. There appears to be a tradeoff of Cobalt (red) for Nickel (green) near the feature while the Gadolinium content (blue) remains relatively uniform.

Figure 12. (a) OIM generated Inverse Pole Figure showing grain orientation for grains belonging to the GdNi-type crystal structure (Cmcm). Black lines indicate boundaries fitting a mirror twin on the $[110]$ plane. (b) Texture of individual pixels confirming preferential orientation near $[010]$ out of the plane of the page. (c) Legend for colors in (a).

technique is not exact enough to determine any epitaxy, but a mirror twin along the $[110]$ directions does have an angular relationship of roughly 37.15° . No indication of the dendrites was noted in the OIM inverse pole figures suggesting a compositional transition only, although small crystallographic fluctuations would be too minor for this technique to notice.

The annealing process has a much greater effect on the microstructure as viewed from the “ xy ” direction. The dendrites coarsen upon annealing becoming regions of nearly homogeneous contrast surrounding the stitches, likely ending at grain boundaries. SEM images of both as-cast, and annealed $x=0.30$ can be seen in Figure 9. While the variations among WDS spectra in the $x=0.00$ and $x=0.15$ matrix regions are relatively low (deviation in Table 1), the values for the $x=0.30$ have a large range with most variation coming from the AC sample. Further analysis of the AL sample of $x=0.30$ is needed, but the persistence of the stitches, changes in dendrites, and coarsening of 1:2 phases are noted.

4. Conclusions

The results of this investigation using SEM, EDS/WDS, and OIM in conjunction with the XRD analyses show that in $\text{GdNi}_{1-x}\text{Co}_x$ alloys the solid solution with the CrB-type crystal structure is indeed terminated at approximately $x=0.45$ (22.5 at.% Co). Excess Nickel and Cobalt are rejected from the matrix and form the $\text{Gd}(\text{Ni},\text{Co})_2$ compound in all compositions up to $x=0.3$. Annealing has a distinct effect on the feature size and shape and on the overall homogeneity of the samples. Microscopy confirms the $x=0.50$ composition to be past the solid solution forming a second major (≈ 50 vol%) phase alongside the 1:1-type phase in a eutectic microstructure. GdCo ($x=1.00$) exhibits a dendritic microstructure with two main , expected phases, and a third unexpected phase not present in the literature. The expected phases are the 1:2 and 4:3 phases; the third was identified as nearly Gd_2Co by WDS though further analysis is needed.

The substitution of Co into the GdNi crystal structure produces interesting microstructural features, particularly in the $x=0.30$ samples, termed “tiger stripes” and “stitches,” depending upon the direction of viewing. When viewed from the yz direction large elongated grains with tiger stripes are seen. These stripes are either too fine, or vary too little in composition to be characterized quantitatively through EDS. Upon viewing the xy direction, the microstructure appears quite different with dendritic regions emanating from the stitches. EDS point analyses suggest a higher concentration of Co in the dendrites than in the matrix, and less Co at the stitches while a linescan both agrees with this and indicates a diffusional segregation of Co during solidification. These unforeseen variations in the microstructure may have a significant effect on the anisotropic magnetic properties of GdNi -based alloys that are generally not expected to be noticeable in polycrystalline materials, and are likely responsible for the very broad Bragg peaks present in the as-cast sample XRD patterns. Upon annealing the Bragg peaks sharpen as expected, and the dendrites coarsen significantly and in some cases disappear.

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(b)

[001]

0 1 0

0 0 1

1 0 0

(c)

0 1 0

0 0 1

1 0 0