

Time and orientation dependence of ordering in anodized aluminum for self-organized magnetic arrays

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Anodization experiments to create alumina pores were performed using pure Al and hard disk Al–Mg substrates. A single step anodization was employed for up to 40 h to determine the time dependence of pore ordering. The pores formed from the Al–Mg substrate were unordered, while ordered-pore domains as large as $3\ \mu\text{m}$ form in both the as-rolled and annealed pure Al samples. The effect of the aluminum grain crystallographic orientation was investigated via orientation-imaging microscopy for the pure Al surface with both order and disordered pores. It was found that neither heat treatment nor crystallographic orientation played a large role in the pore ordering. © 2000 American Institute of Physics. [S0021-8979(00)35308-7]

I. INTRODUCTION

As the magnetic recording areal density approaches 40 Gbit/in.², the thermal stability effect becomes a more conspicuous issue.¹ To overcome the superparamagnetic limit while maintaining a good signal to noise ratio, high anisotropy materials such as $L1_0$ -phased CoPt, $\text{Fe}_{14}\text{Nd}_2\text{B}$ or SmCo_5 are being studied for future applications.² However, the current limit of the head field generation¹ may prevent these materials from entering the magnetic recording industry for some time.

Another approach is to fabricate each bit cell into ordered single isolated magnetic units.³ This method could scale the dimension of the bit cell down to the superparamagnetic limit, which is determined only by the energy barrier to magnetic reversal. e -beam and laser lithography are two current approaches to make well defined arrays of small features.^{4,5} Another method, anodization of aluminum, is a simple and low cost process, which provides nanometer-scaled close-packed hexagonal arrays of alumina/aluminum pores.^{6,7} This highly ordered arrangement gives rise to a promising potential to synthesize hexagonal patterns of self-organized magnetic arrays (SOMA) for ultrahigh magnetic recording.^{8,9}

Though the mesoscopic phenomenon of the pore ordering is not fully understood, it has been experimentally demonstrated that the duration of the anodization and the initial surface condition is critical to the scale of the ordering.⁶ Recently Konovalov *et al.*¹⁰ reported that the crystallographic orientation of aluminum single crystals strongly affects the surface morphology in electropolishing. Hence, it is important to know the effect of all the variables in the process including heat treatment, polishing, anodization, pore-widening, etching, etc., in order to synthesize hexagonal arrays with extended long-range order.

When grown on a pure aluminum surface, the alumina is very densely packed. This may contribute to the ability to form a hexagonal pore when aluminum is anodized to alumina. Hence, until this work, it has not been determined if pores could be created on Al alloys. However, pure aluminum is far too soft to be used as a hard disk substrate. Here, we report the anodization of the Al–Mg (5000 series alloy)

hard disk substrate. We have also studied the effect of heat treatment, anodization time, and crystallographic orientation on the pore ordering from pure aluminum by using scanning electron microscope (SEM) and orientation imaging microscope (OIM).

II. EXPERIMENT

Al–Mg coupons cut from a hard disk substrate and 99.99% pure Al coupons cut from a 1 mm thick foil were mechanically polished using a Leco (spectrum 2000 system) polisher with three different size of alumina powder $3\ \mu\text{m}$, $0.3\ \mu\text{m}$, and $0.05\ \mu\text{m}$, and then thermally annealed at $550\ ^\circ\text{C}$ for 24 h in air. Prior to anodizing, electropolishing in a perchloric acid–ethanol mixture at 12 V was employed to develop a reproducible super flat surface finish. One step anodizing was adopted to simplify the process and exclude the effect of pretexturing.^{6,7} This anodizing step was performed at a constant voltage in 0.23 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). After rinsing, the anodized coupon was placed in 0.2 M phosphoric acid (H_3PO_4) for pore widening. To study the final pore ordering the porous alumina was etched off in a mixture of 0.2 M chromic acid (H_2CrO_4) and 0.4 M H_3PO_4 . All of the above experiments were carried out at room temperature. A Philips XL30-FEG SEM was used for the morphology observation. Another Philips XL30-FEG SEM with OIM facilities was used to determine the crystallographic orientation of each aluminum grain.

III. RESULTS AND DISCUSSION

We found that Al–Mg coupons can be electropolished into very shiny flat surfaces under similar conditions to those used for the pure aluminum samples. Figure 1 shows the final surface condition of an Al–Mg coupon after anodizing and etching. Since the alumina has been etched off, the white portions of the SEM image show the highest topological areas of the surface plane, while the dark regions represent the pores. The two samples in Figs. 1(a) and 1(b) were anodized for 20 h at 30 V and 40 V, respectively. The pore cell size of sample (a) is 70 nm, sample, (b) 100 nm. The voltage dependence of the pore cell size is about 3 nm/V, which is close to

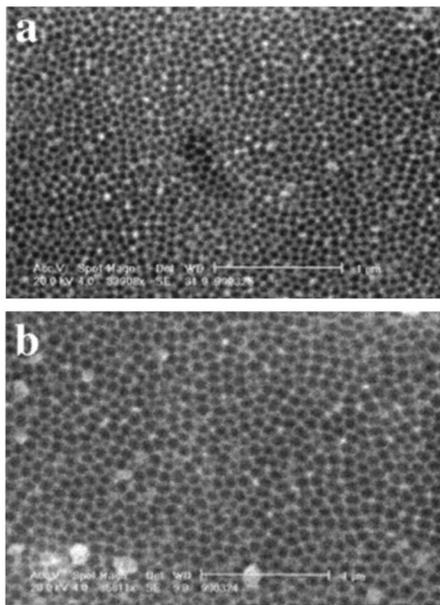


FIG. 1. SEM image of Al-Mg surfaces after anodizing and etching. They were anodized at (a) 30 V, (b) 40 V.

that of the pure aluminum case.¹¹ However, unlike the pure aluminum results, no observable long-range ordering was achieved when using the same anodizing conditions as for pure aluminum. This difficulty in obtaining ordering pores may be due to the small inclusions of Mg and Mn in the 5000 series alloy.

For comparison, Figs. 2(a)–2(c) show the surfaces of as-rolled pure aluminum samples after anodizing at 40 V for 10 h, 20 h, and 40 h, respectively. Figures 2(d)–2(e) show

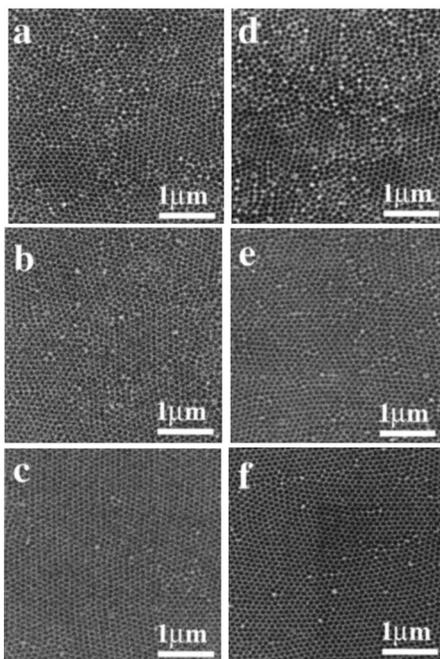


FIG. 2. (a), (b), (c) surface of as-rolled pure aluminum sample after anodizing at 40 V for 10 h, 20 h, 40 h, respectively. (d), (e), (f) surface of annealed pure aluminum sample after anodizing at 40 V for 10 h, 20 h, 40 h, respectively.

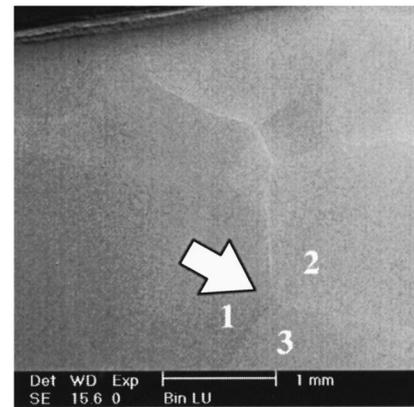


FIG. 3. SEM image of an annealed pure aluminum sample after anodizing and etching.

the surfaces of annealed pure aluminum samples after anodizing at the same conditions for 10 h, 20 h, and 40 h, respectively. It can be seen that heat treatment makes no difference between the two sets of samples, although the average grain size, about 2 mm, of the annealed samples is more than ten times larger than that of the as-rolled sample. The time dependence of the pore ordering is quite obvious. The average ordered pore domain size increases from 0.5 μm to 3 μm as the anodizing time is increased from 10 h to 40 h. It should be noted that the ordered-pore domain size is limited by stability of the system. Prolonging the anodization time does not increase the domain size.

In order to better understand the role of crystallographic orientation upon the ordering and pore growth a pure alumi-

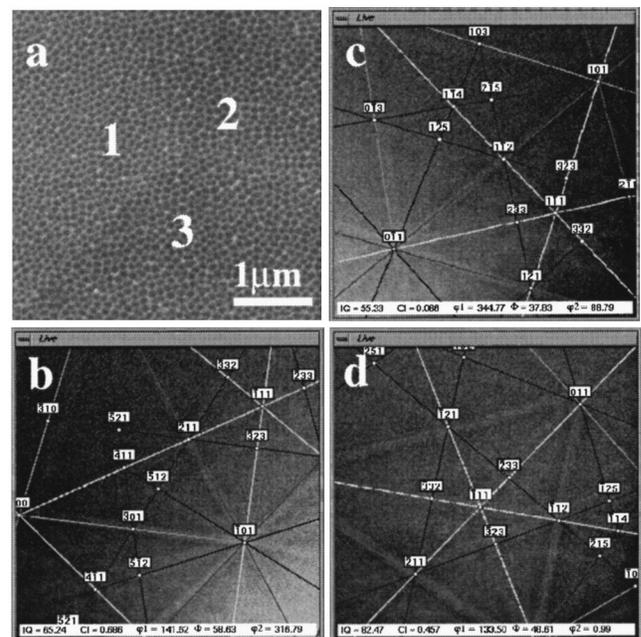


FIG. 4. (a) SEM image shows random pore growth in the pure aluminum surface and a triple junction area same as the one in Fig. 3; (b), (c), (d) electron back scattering diffraction (EBSD) patterns corresponding to the grains 1, 2, 3 in (a), respectively. The Euler angles of the three grains are determined as (b) $\varphi_1 = 141.62$, $\Phi = 58.63$, $\varphi_2 = 316.79$; (c) $\varphi_1 = 344.77$, $\Phi = 37.83$, $\varphi_2 = 88.79$; (d) $\varphi_1 = 133.50$, $\Phi = 48.61$, $\varphi_2 = 0.99$.

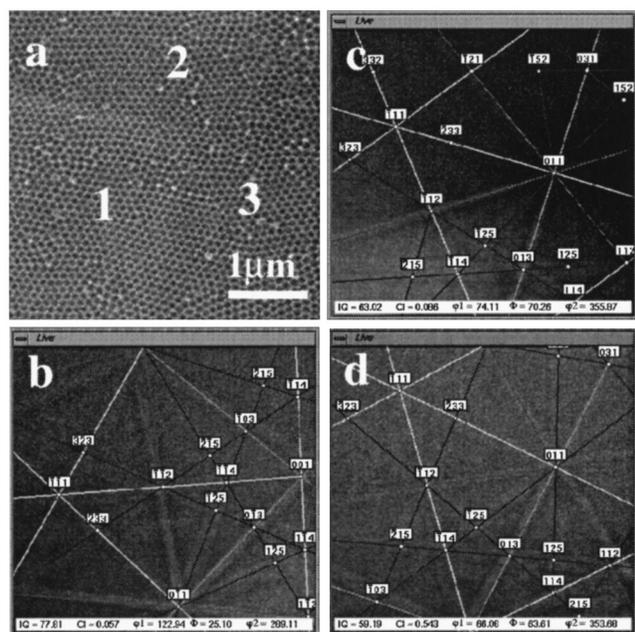


FIG. 5. (a) SEM image showing ordered pore growth in the pure aluminum surface and a triple junction area; (b), (c), (d) EBSD patterns corresponding to the grain 1, 2, 3 in (a), respectively. The Euler angles of the three grains are determined as (b) $\varphi_1 = 122.94$, $\Phi = 25.10$, $\varphi_2 = 289.11$; (c) $\varphi_1 = 74.11$, $\Phi = 70.26$, $\varphi_2 = 355.87$; (d) $\varphi_1 = 66.08$, $\Phi = 63.61$, $\varphi_2 = 353.68$.

num sample was deliberately surface treated so that the pores grew in a random arrangement. Figure 3 is a low magnification SEM image of an annealed pure aluminum sample after anodizing and etching. The contrast in the image is the crystallographic-orientation contrast contributed by back scattering electrons. The white arrow indicates a crystalline triple junction area consist of three grains of different orientations. The exact orientation of each grain referenced to the SEM coordinate system can be determined precisely based on the electron back scattering diffraction (EBSD) patterns collected and identified by the OIM.¹² It can be seen from the high magnification image [Fig. 4(a)] that the large angle grain boundaries have little effect on the random pore growth. Figures 4(b)–4(d) show the EBSD patterns corresponding to the individual grains 1, 2, 3, respectively. From the three Euler angles of each grain (see the bottom line), it can be estimated that the misorientations between the three grains are larger than 30° .

Figure 5(a) shows a triple junction area of an anodized pure aluminum surface with ordered pore domains. The orientation of the grains 1, 2, and 3, are shown in Figs. 5(b)–5(d), respectively. From both the EBSD patterns and the Euler angles, it can be seen that there is only a small misorientation between grains 2 and 3, while that the boundaries between grains 1–2 and 1–3 are large angle grain boundaries. This is consistent with the contrast in the SEM

image [Fig. 5(a)], which shows that grain 1 is brighter than grain 2 and 3, and that the grain boundary between grain 2 and 3 can hardly be discerned. Figure 5(a) also shows that the ordered domains pass through the 1–2 and 1–3 boundaries with little disturbance. On the other hand, there happened to be some disordered pores right at the low angle boundary 2–3. Therefore, it can be concluded that the crystallographic orientation of the aluminum grains has little effect on the pore ordering.

IV. CONCLUSION

When an Al–Mg alloy, used for hard disk substrate, is anodized random disordered pores results. The voltage dependence of the pore cell size is similar to the pure aluminum case. Using a one step anodizing method, the time dependence of the pore ordering in pure aluminum samples has been observed up to 40 h yielding ordered pore domains, whose sizes are as large as $3 \mu\text{m}$. Preanodization heat treatment of as-rolled Al sheets has little effect on pore ordering independent of aluminum grain coarsening. The orientations of the aluminum grains have been studied using OIM and the crystallographic orientation has been found to have little effect on the pore ordering.

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