Supporting Information

Simulations of cracks supported by experiments: The influence of the film height and isotropy on the geometry of crack patterns

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Experimental Method

Chemicals. Iron (II) chloride $Fe(Cl)_2$ and iron (III) chloride $Fe(Cl)_3$ were from Prolabo. Dodecanoic acid, $CH_3(CH_2)_{10}COOH$ and ammonium hydroxide, NH_4OH were from Aldrich.

Apparatus. A JEOL (100kV) model JEM-1011 transmission electron microscope (TEM) was used to characterize the size of γ -Fe₂O₃ nanocrystals. The directional cracks were produced with an electromagnet (Oxford Instruments N38). The crack patterns are visualized with a scanning electron microscope (SEM) JEOL 5510 LV and with a C-740 Olympus digital camera.

Synthesis of Solutions of Maghemite Nanocrystals. The γ -Fe₂O₃ nanocrystals are synthesized according to the well-known synthesis method described elsewhere¹ with slight changes. An acidic aqueous mixture of iron (III) chloride, FeCl₃ (80 ml, 1M) and iron (II) chloride, FeCl₂ (20 ml, 2M, 2M HCl) is added to an ammonium hydroxide solution, NH₄OH (800 ml, 0.6 M). At this stage, uncoated nanocrystals are produced. Two different procedures are used to coat the nanocrystals depending on the solvent.

(i) The procedure used for coating with citrate ions is as follows: The precipitate is washed with an acidic aqueous solution of nitric acid, HNO₃ (10^{-2} M) until a solution at pH = 2 is reached. Sodium citrate, Na₃C₆O₇H₅ (1.5 x 10^{-2} M), dissolved in water is added to the solution, which is stirred for 30 minutes at 90 °C, and the nanocrystals precipitate on addition of acetone. After washing with a large excess of acetone, the powder is dried in air and the particles coated with citrate ions are dispersed in water, to give an aqueous ferrofluid.

(ii) The procedure used for coating with dodecanoic acid is as follows: The precipitate of uncoated nanocrystals is washed with a large excess of ethanol. Then a solution of dodecanoic acid, $CH_3(CH_2)_{10}COOH$ (0.5M), solubilized in ethanol, is added. The solution is sonicated for 2 h at 90 °C. The resulting precipitate is washed with a large excess of ethanol, and the powder is dried in air. The nanocrystals coated with dodecanoic acid are dispersed in chloroform, to give an oily ferrofluid.

The γ -Fe₂O₃ nanocrystals have an average diameter and polydispersity of 10 nm and 25%, respectively.

Fabrication and Analysis of Crack Patterns.

A solution of γ -Fe₂O₃ nanocrystals dispersed either in water or chloroform is injected above a silicon wafer placed at the bottom of a glass beaker at room temperature. Crack patterns are formed during the drying of the ferrofluid. After complete evaporation of the solvent, the crack patterns are visualized with a scanning electron microscope (SEM) and with a digital camera depending on the size of the crack patterns. The area analysis of the individual fragments bounded by cracks is made by using a public domain image processing and analysis program (NIH Image)² on about 100 and 600 fragments on average. The heights, *h*, of the nanocrystal film are measured over the whole substrate on tilting by 45°. The layer height of the crack patterns is controlled by solutions containing 2% to 43% by weight of nanoparticles and 0.2 ml to 27 ml in volume before drying. Samples with average layer heights, *h*, varying from 1 μ m to 200 μ m are obtained using a 6 x 6 mm² silicon wafer. For thicker samples up to 1000 μ m as average layer height, we used either a circular (75 mm-diameter) or a square (25x25 mm²) silicon wafer.

The scaling of the average crack distance in experiments.

We will now summarize the scaling of the crack distances observed in the experiments and compare these results to the theoretical predictions in section 3.2.

Since some crack generations do not appear in very thin films, we need to define primary 1D and 2D cracks and secondary 2D cracks as explained in (3,4). In the directional case, the straight cracks parallel to the direction of the applied field correspond to the first generation of cracks and are called primary 1D cracks. The fragments bounded by these primary 1D cracks and the perpendicular ones (second generation of cracks) are called primary 2D cracks. The mean crack aperture of parallel cracks (first generation of primary 1D cracks) is about twice as large as that of the perpendicular ones (second generation of cracks). At the end of the drying process, the crack patterns at larger film heights show that the primary 2D crack fragments are broken into smaller ones (from 2 to 8 domains) corresponding to the third and later generations of cracks. These new generations of cracks are called secondary 2D cracks.

To analyze the isotropic 2D crack patterns, we use the same criterion as for directional cracks to separate the primary cracks from the secondary ones. Thus, all cracks with an aperture three to six times smaller than those of the two first cracks are called secondary 2D cracks.

Let us first summarize the observations of our recent publications [49,50]. In the case of isotropic stress, a linear variation, on a logarithmic scale, of the average square root area of primary crack domains ($\sqrt{A_{ip}}$), ignoring secondary cracks as explained above, with the layer height was observed experimentally (solid circles in Fig. 4). Using the average experimental value of the dimensionless ratio $K = \sqrt{A_{ip}} / h (K = 5.42 \pm 0.32)$, the linear fit gives a slope of 0.98 ± 0.01 in good agreement with the scaling law, $\sqrt{A_{ip}} \approx Kh$. In the directional case, a linear variation of the average crack distance (D) between primary (1D) cracks with the corresponding height (h) is observed on a logarithmic scale (open squares in Fig. 4). Using the average experimental value of the dimensionless ratio K = D/h ($K = 5.31 \pm 0.25$), the linear fit gives a slope of 1.00 ± 0.01 in good agreement with the scaling law, $D \approx Kh$. The same linear variation behaviour $\sqrt{A_{lp}} = Kh$ was observed for the average square root area fragments of the directional primary 2D crack domains defined above and denoted by $\sqrt{A_{lp}}$ with the layer height (Fig. 4). The K values obtained for the 1D and 2D cracking systems were equal within the experimental errors $(5.31 \pm 0.25 \text{ and } 5.42 \pm 0.32)$. Hence, the magnetic field induces the formation of regular directional crack patterns without any effect on the Kfactor.

To investigate the scaling also for the secondary cracks, we carried out a study using the area fragments of the secondary directional (A_{1s}) and, here, isotropic (A_{is}) 2D crack domains. Surprisingly, the variations of the average square root area fragments of the secondary 2D crack domains denoted by $\sqrt{A_{1s}}$ and $\sqrt{A_{is}}$ as a function of the layer height (open triangles and circles in Fig. 4) also follow a linear scaling as do the primary cracks with a slope of 0.99 ± 0.01 (dashed line in Fig. 4). Note that the origin of the plot differs for the primary cracks and the secondary ones. The dimensionless ratio *K* differs by a factor of two between the primary cracks ($K = 5.31 \pm 0.25$) and the secondary ones ($K = 2.66 \pm 0.21$). This leads to a linear relationship $\sqrt{A_{1s}} \approx \sqrt{A_{is}} \approx 0.5 D$. Hence, the length scale of the pattern for secondary cracks is divided by a factor of 2 compared to the primary cracks.

References

(1) Massart, R. IEEE trans. on Magn. MAG 1981, 17, 1247.

(2) NIH *Image* is a public domain image processing and analysis program for the Macintosh : http://rsb.info.nih.gov/nih-image/about.html.

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- (4) Ngo, A. T.; Richardi, J.; Pileni, M. P. J. Phys. Chem. B 2008, 112,14409.