Self-avoiding magnetic chains formed in annealed Fe-Cu multilayers: experiment and simulation

1991 J. Phys.: Condens. Matter 3 4165

(http://iopscience.iop.org/0953-8984/3/23/005)

J. Phys.: Condens. Matter 3 (1991) 4165–4171. Printed in the UK

Self-avoiding magnetic chains formed in annealed Fe–Cu multilayers: experiment and simulation

C H Shang, H D Li and B X Liu†
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, *People's Republic of China*

Received 23 April 1990, in final form 1 February 1991

Abstract. Self-avoiding magnetic chains (SAMCs) were observed in annealed Fe–Cu multilayers. Scaling analyses showed that these structures were statistically self-similar and satisfied the power-law relationship well in their stretched dimension. Compared with the self-avoiding walks, the SAMCs were found to have smaller global fractal dimensionality and less geometrical entropy, which were attributed to the existing magnetic interaction and local lattice coherence during their growth, respectively. A modified tip-to-tip model was proposed to simulate the aggregation processes, and the results were in agreement with the observations.

1. Introduction

Through the years, self-avoidance has been studied intensively in several fields, including self-avoiding walks (SAWs) and continuum limits of gauge theories [1]. It has recently been recognized that SAW-like structures can be formed in aggregation processes with a dipole magnetic interaction [2]. Nonetheless little information at present is known about such magnetic chains, especially those formed in thin solid films. As is known, a variety of factors, such as stresses, surface diffusion and lattice coherence, will incorporate and influence the aggregating behaviour. Consequently, the aggregation processes in thin solid films must be much more complicated than those in other relevant problems, such as dielectric breakdown and viscous fingering [3]. This notwithstanding, thin solid films have proved [4] to be the favourable environments for forming many novel patterns such as dendritic crystals and ramified fractals.

In this study, Fe–Cu sandwich multilayers were chosen as the material in which to investigate the possibility of forming magnetic chains. Low-temperature thermal annealing was also conducted to enhance the aggregating processes in the multilayered films. The Fe–Cu system is of interest because iron is a ferromagnetic element of maximum atomic Bohr magneton, while copper is a typical paramagnetic element. Also, Fe and Cu are immiscible even in the liquid state [5], meaning that Fe and Cu atoms are repulsive, and neither solid solutions nor equilibrium compounds can readily be formed. This paper reports the observation of self-avoiding magnetic chains (SAMCs) in the

† Also at Center of Condensed Matter and Radiation Physics CCAST (World Laboratory) PO Box 8730, Beijing, People's Republic of China.

0953-8984/91/234165 + 07 $03.50

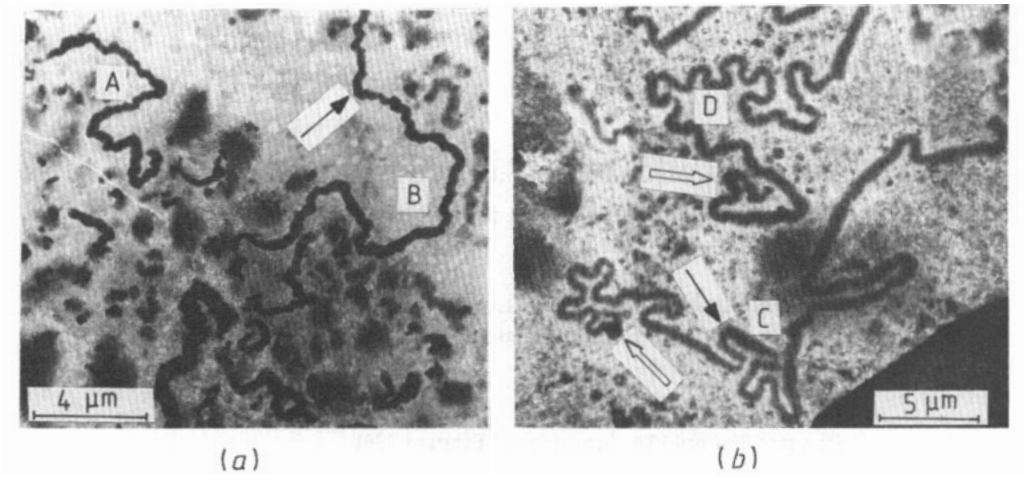

Figure 1. SAMCs observed in Fe–Cu multilayers annealed at (*a*) 100 °C and (*b*) 400 °C for 2 h.

thermally annealed Fe–Cu films. Their scaling properties and pertinent microstructures are presented in detail. The experimental observations are also compared with our computer simulation results.

2. Experimental details

Thin Fe–Cu multilayered films were prepared by alternatively depositing pure metals onto cleaved NaCl substrates in a high-vacuum electron gun system. Samples consisted of three layers of copper and two layers of ferromagnetic element Fe with a total thickness of 45 nm. The overall composition of the films was designed to be about $Fe_{50}Cu_{50}$ and realized by adjusting the relative layer thicknesses of two constituents. Thermal annealing was performed for the deposited films from 100 to 400 °C in a vacuum of better than 5×10^{-6} Torr. At each temperature, the annealing time was 2 h. Self-supported films were obtained by dissolving NaCl substrates in deionized water and then placed onto Mo grids for transmission electron microscopy (TEM) (H-800 and JEM 200-CX) examination. *In situ* energy dispersive spectroscopy (EDS) was also used to determine the local composition of the resulted structures.

3. Results and discussion

TEM bright-field examination showed that many chain-like structures of dark appearance emerged in the annealed films. The most conspicuous feature of these chains was self-avoidance. Figure 1(*a*) and figure 1(*b*) are two typical examples of the self-avoiding chains observed in the films annealed at 100 °C and 400 °C, respectively. It is evident that the lateral sizes of the chains differ largely even for those developed at the same temperature, e.g. chains A and B in figure 1(*a*). However, the width of a chain seems to be constant although some local fluctuations can exist. Furthermore, a chain with a width of about 1 μm may stretch to a dimension of several tens of micrometres. The

linear dimension of chain C in figure 1(*b*), for instance, is about 25 μm, while its average width is 0.6 μm. It should be pointed out that such chains are confined to thin films with a thickness of less than 50 nm. To this end, the chain-like structures can be regarded as two-dimensional aggregates and can be reasonably approximated by ideal curves.

Scrutiny of figure 1 indicates another underlying feature, i.e. that a chain usually turns abruptly with some specific angles, such as $\pi/4$ and $\pi/2$, as indicated by the black arrows. Unlike the clusters of diffusion-limited aggregation (DLA) [6], the self-avoiding chains in our case are therefore not entirely random and inherit some order information instead. One can find from figure 1 that the chains formed at higher temperatures usually manifest themselves as longer and more complicated structures with a number of smooth turns. *In situ* EDS measurement indicated that the content of the magnetic element Fe on a dark chain was about 60–70 at.%, higher than that in the matrix (about 50 at.% Fe). Electron diffraction showed that there were only crystalline Fe and Cu in the films. The microbeam diffraction analysis also showed that sharp diffraction spots of BCC iron could be detected along a chain, and their patterns changed occasionally. This means that each dark chain is composed of polycrystalline particles of the ferromagnetic element Fe. This is the very reason why a chain turns at some intrinsic angles possessed by a BCC lattice. Another striking feature is that a developed chain always has one of its ends surrounded by its own trap, as indicated by the white arrows in figure 1(*b*).

To unravel the scaling properties of these novel SAMCs, the corresponding electron micrographs were digitized with a VAX image processor at a resolution of 512 × 512 pixels. The lower cut-off during the image processing corresponded to the average width (about 10 pixels) of a chain, and the upper cut-off was its stretched dimension. For a linear fractal, its relative length $L(\delta)$ in the scale of δ should satisfy the following power law [7]:

$$L(\delta) \propto \delta^{-D}. \tag{1}$$

As shown in figure 2, for instance, all experimental data for the labelled chains in figure 1 can be well fitted by straight lines. Such scale invariance holds true for all digitized chains, of which the lateral sizes ought to be 20 times longer than their corresponding average widths so as to have good statistics. Obviously, the fitting lines obtained for chains A and B in figure 1(*a*), or chains C and D in figure 1(*b*), are parallel to each other, respectively. The fractal dimension evaluated by least-squares fit for chains A (and B) and chains C (and D) were 1.13 and 1.29, respectively, with a reasonable uncertainty of ±0.06. The experimental results show that the same wide chains formed at the same temperature almost share a common value of fractal dimension within the experimental error bar. The fractal dimensionality extracted from the density correlation function [7] (i.e. $C(r) \propto r^{\alpha}$ and $\alpha = 2 - D$) of a chain also confirmed the results from equation (1) within the experimental uncertainty. For instance, the codimension α for chain C in figure 1(*b*) was calculated to be 0.70 ± 0.06. The fractal dimensions for the chains 300 nm and 500 nm wide formed at temperatures 200 °C and 300 °C were found to be about 1.20 and 1.25, respectively. In the computation, each dimensionality was averaged over at least four digitized chains formed at a same temperature. The above results indicate that for the chains of nearly the same width the fractal dimensions increase with increasing annealing temperature. This tendency can be understood in the light of the previous results of magnetic aggregation [2]. Because increasing temperature can relatively reduce the magnetic interaction, the disruptive randomness will contribute more and finally leads to an increase in fractal dimensionality [8]. Qualitatively, such a result is in accordance with the fact that the chains formed at higher temperatures usually manifest

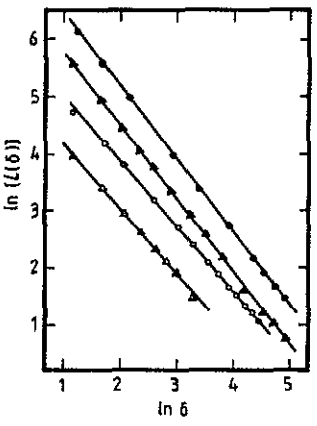

Figure 2. Log–log plots in the fractal analyses for the labelled chains in figure 1: △, chain A; ○, chain B; ●, chain C; ▲, chain D. The fractal dimension D_c for chain A (and B) is 1.13 ± 0.06, and for chain C (and D) is 1.29 ± 0.06.

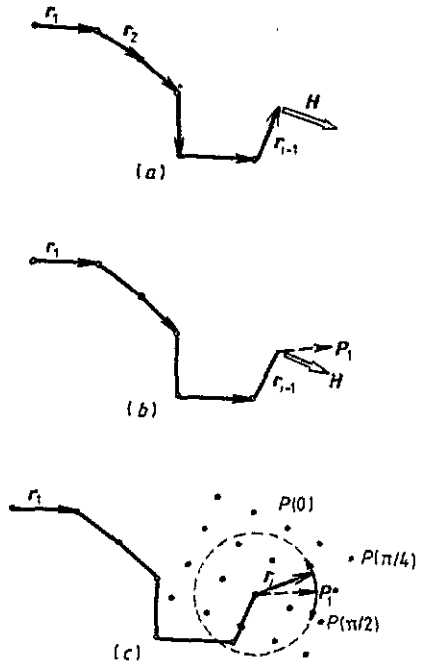

Figure 3. Sketch map of the modified tip-to-tip model: (*a*) magnetic field; (*b*) primary orientation P_1; (*c*) rotational diffusion and differential sticking probability.

themselves as more complicated structures with a number of smooth turns, as shown in figure 1. By comparison, similar temperature dependence of fractal dimensionality on the annealing temperature was also recently reported [9] for the highly ramified fractals.

Real aggregation processes in thin solid films involve many physical interactions. As for the self-avoiding chains in our case, there are at least three important factors that are known to affect the formation processes. They are

(i) magnetic interaction,
(ii) local lattice coherence during the growth of magnetic chains and
(iii) atomic diffusion.

Microscopically, the immiscibility of two constituent elements implies that the Fe and Cu atoms tend to repulse each other. Furthermore, the as-deposited films were at a higher energetic state than the bulk materials. During the subsequent relaxation to the equilibrium state, the two repulsive atoms are expected to separate into some unique forms. Additionally, elevating the temperature and the interfacial structure may considerably enhance the atomic diffusion and the growth of these open chains. In the experiments, however, only Fe crystalline chain-like aggregates were observed in the films, but they were not observed otherwise. These suggest that the formation of self-avoiding chains essentially results from the magnetic interaction of ferromagnetic Fe. In fact, several workers have noticed that magnetic particles always organized themselves into chain-like structures [10], and that increasing the magnetization (i.e.

effective strength) would increase the tendency to form open chains [2], i.e. to induce the self-avoidance.

The formation picture of the observed magnetic chains was thought to be analogous to a walker proceeding along SAW [1] trajectories. It indicates that a chain of certain width will naturally stop its growth if the active end falls into its own trap, and this is exactly the case in our observations. In the practical trap, the neighbouring dipoles on the chain were all exhausted in the previous growth, and their screen effects further prevented the Fe atoms from diffusing in. Thus, a developed chain always had one of its ends surrounded by its dead trap, as indicated in figure 1. Concerning the aggregating particles during the pattern formation, we think that they are most likely to be atomic Fe, because the diffusion of polycrystalline particles (say several hundred nanometres in size) in thin solid films is hardly expected. From a metallurgical point of view, the growth of polycrystalline chains via atomic diffusion can be regarded as a recrystallization process in the annealed films, and the resulting polycrystals on the chains can also be visualized as individual dipoles.

According to the above discussion of the formation processes of the SAMC, two-dimensional computer simulation was carried out for the rigid magnetic dipoles, having a basis similar to that of tip-to-tip model [11]. However, in the simple tip-to-tip model, no diffusion (either translational or rotational) was allowed. In our modified model, the dipolar interaction among the moments was included through a Monte Carlo approach [8] to influence the primary orientation $\boldsymbol{P}_1$ of a dipole, as sketched in figures 3(*a*) and 3(*b*). The primary orientation $\boldsymbol{P}_1$ was selected to minimize the dipole interaction energy in more than ten trials. The dispersion between direction $\boldsymbol{P}_1$ and that of local magnetic field strength $\boldsymbol{H}$ was mainly ascribed to the thermal fluctuation. After each tip attachment the Brownian rotational diffusion was carried out around the selected direction, as shown in figure 3(*c*) by the gyration cycle. Rotation of a dipole about its attached tip (the point O here) terminated in the most probable crystallographic directions after a given time. By the most probable crystallographic direction, we mean that crystal direction that makes the quantity $n_\theta P(\theta)$ take its maximum value, where n_θ is the number of rotational orientations $\boldsymbol{P}_1$ acquiring a specific orientation θ, and $P(\theta)$ is the sticking probability associated with the lattice symmetry of aggregating particles. In figure 3(*c*), we take an example of the {100} crystal band of the BCC lattice. Differential sticking probabilities are also considered to form different elemental units, as shown in figure 3. The self-avoidance was imposed through the assumption that an intersection would cause an infinite increase in elastic energy and thus be discarded. A growing chain would naturally cease its growth if its active end fell into its own trap, where any further growth would induce an intersection. Figure 4(*a*) shows two typical chains (E and F) simulated under different conditions. Chain E is a typical aggregate with a dipolar interaction K_{dd} of 1000. The sticking probabilities of forming a segment, a right angle and a $\pi/4$ wedge were assigned to be $P(0) = 0.5$, $P(\pi/2) = 0.2$ and $P(\pi/4) = 0.15$, respectively. The fractal dimension, as indicated in figure 4(*b*) (full triangles), was determined according to equation (1) to be $D_c = 1.14 \pm 0.06$. Chain F is an alternative case under the conditions $K_{dd} = 800$, $P(0) = 0.3$, $P(\pi/2) = 0.1$ and $P(\pi/4) = 0.2$. Its fractal dimension was found to be $D_c = 1.27 \pm 0.06$. By properly selecting the parameters, the simulated clusters could well approach real clusters, not only in fractal dimensionality but also in overall topological characteristics, such as dead traps, and smooth turns at high temperatures. We simulated more than 100 clusters under different conditions and found that, at nearly the same sticking probabilities, the fractal dimensionality of self-avoiding chains tended to decrease as the interaction strength increases (i.e. equivalent to elevating the

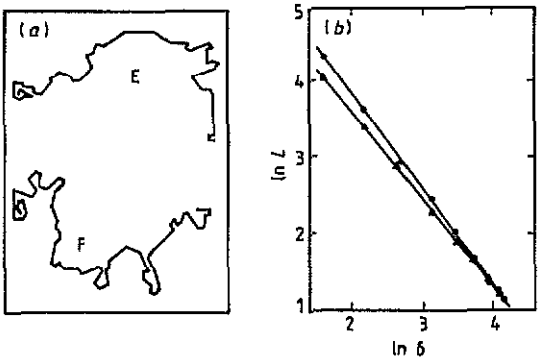

Figure 4. (*a*) Typical simulated chains with dipolar interactions, where differential sticking probability and rotational diffusion are also considered: chain E, 82 particles, $K_{dd} = 1000$, $P(0) = 0.5$, $P(\pi/2) = 0.2$, and $P(\pi/4) = 0.15$; chain F, 111 particles, $K_{dd} = 800$, $P(0) = 0.3$, $P(\pi/2) = 0.1$, $P(\pi/4) = 0.2$. (*b*) Log–log plot of the relative length versus the measuring scale for the above chains: ▲, chain E; ●, chain F. The fractal dimension for the chains E and F are evaluated by least-squares fit to be 1.14 and 1.27, respectively.

annealing temperature), as shown in figure 4. However, because the sticking probabilities were slightly influenced by the magnetic interaction, therefore it was difficult to depict a quantitative relationship between fractal dimensionality and dipole interaction strength in the framework of the present model.

From the above simulation and the real morphology in figure 1, one can see that the SAMC aggregates are quite analogous to the case of SAWs. For the SAWs in two-dimensional space, it has been proved that there exists a universal fractal dimensionality of $D_f = \frac{4}{3} = 1.33$. Different from the SAW model, the first characteristic of the observed SAMCs is the existing dipole magnetic interaction during the chain growth. It has been proved [2, 10] (by both experiments and simulations) that such long-range interaction may effectively reduce the fractal dimension of the ramified aggregates. Obviously, such an inference seems to be valid for the self-avoiding structures as well. Both our experimental results and computer simulation are reasonably constrained below and approaching the value ($D = 1.33$) of the SAW as the magnetic interaction relatively weakens. The second distinguished feature from the SAW is the macroscopic lattice information of magnetic chains. It indicates that the observed SAMCs are less random or have lower entropy than the SAWs. Our computer simulation also demonstrates that the effect of local lattice coherence does not alter the global fractal dimension of the self-avoiding structures.

4. Conclusion

Two-dimensional SAMCs, composed of polycrystalline particles of BCC iron, were formed in Fe–Cu multilayered films after appropriate thermal annealing. Unlike the DLA [6] structures, the observed chains were not entirely random and usually turned at some intrinsic angles relevant to the BCC Fe lattice. Compared with the SAW model, the observed structures were characterized by the reduced fractal dimensions and less geometric entropy. In our computer simulation, the lattice coherence of aggregating particles was firstly taken into consideration for the dipolar aggregation, and the simulated clusters under proper conditions could well realize the observed chains.

Acknowledgments

We are grateful to the staff of the TEM Laboratory of Beijing University and the staff of Analysis Center and Image Center of Tsinghua University for their help. We also thank

Mr X Y Cheng for his technical help with the experiment. The financial support from the National Natural Science Foundation of China and from the International Atomic Energy Agency (Research Contract 4731/R3/RB) is gratefully acknowledged.

References

[1] de Gennes P G 1979 *Scaling concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
Kremer K and Lyklema J W 1985 *Phys. Rev. Lett.* **54** 267
[2] Helgesen G, Skjeltorp A T, Mors P M, Botet R and Jullien R 1988 *Phys. Rev. Lett.* **61** 1736
[3] Niemeyer L, Pietronero L and Weismann H J 1984 *Phys. Rev. Lett.* **52** 1033
Lenormand R 1986 *Physica* A **140** 114
[4] Shang C H, Li H D and Liu B X 1989 *Phys. Rev.* B **40** 2733
Liu B X, Huang L J, Tao K, Shang C H and Li H D 1987 *Phys. Rev. Lett.* **59** 745
[5] Chien C L, Liou S H, Kofalt D, Yu W, Egami T and McGuire T R 1986 *Phys. Rev.* B **33** 3247
[6] Meakin P and Witter T. A. 1983 *Phys. Rev.* A **28** 2985
Meakin P 1986 *Phys. Rev.* A **34** 790
[7] Mandelbrot B B 1982 *The Fractal Geometry of Nature* (San Francisco, CA: Freeman)
[8] Mors P M, Botet R and Jullien R 1987 *J. Phys. A: Math. Gen.* **20** L975
[9] Hou J G and Wu Z Q 1989 *Phys. Rev.* B **40** 1008
[10] Niklasson G A, Torebring A, Larsson C and Granquist C G 1988 *Phys. Rev. Lett.* **60** 1735
[11] Jullien R 1985 *Phys. Rev. Lett.* **55** 1697; 1986 *J. Phys. A: Math. Gen.* **19** 2119