Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/S163-04
Chinese Physics
© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

ATOMIC FORCE MICROSCOPY STUDIES AND MODELING OF SURFACE STRUCTURES PATTERNED DURING OSTWALD RIPENING AT Fe/Mo MULTILAYER SYSTEMS*

Shen Dian-hong(沈电洪)[a)†], Luo Guang-ming(罗光明)[a)], Kang Ning(康 宁)[a)], Lai Wu-yan(赖武彦)[a)], A. Berlinger[b)], and P. von Blanckenhagen[b)]

[a)] *Institute of Physics, Chinese Academy of Sciences, Beijing* 100080, *China*

[b)] *Forschungszentrum Karlsruhe, Institut fuer Nanotechnologie, Postfach* 3640 D-76021 *Karlsruhe, Germany*

(Received 20 April 2001)

Fe/Mo multilayers which were grown by sputtering, annealed in high vacuum and analyzed by means of Atomic Force Microscopy and Scanning Electron Microscopy. Concentric circle-1ike patterns were observed after annealing. Two-dimensional Ostwald ripening mechanisms in immiscible systems of Fe/Mo may explain the formation of these structures. We simulated pattern formation in a late stage of the phase separation by applying the Thomas-Freundlich thermodynamic relation. Based on a two-dimensional mode1 in the framework of the Lifshitz-Slyozov theory, our modeling has been extended to include the diffusion limitation in a multi-cluster system.

Keywords: AFM, multilayer, Ostwald ripening
PACC: 6116P, 6800, 8110

I. INTRODUCTION

Recently, Fe/Mo multilayers which are modulated homogeneously with an interlayer distance in the range of one to two nanometers were found to exhibit the giant magnetic resistance (GMR) effect.[1] The Fe/Mo system is an immiscible binary alloy. The study of the thermal stability of multilayer systems is important for optimizing the preparation process as well as the conditions for applications. It was found that the Fe/Mo multilayer system shows the phenomenon of phase separation after annealing at higher temperatures. The process of phase separation ends in the formation of concentric circle-like patterns on the surface of the sample. It is of interest to understand what kind of mechanism leads to such a surface pattern. In a previous study of the Fe/Mo system, the layered structure could be visualized partly by analyzing with an atomic force microscope(AFM) the wall of a shallow crater at the surface of the multilayer system produced by ion sputtering.[2]

Generally, the process of phase separation has two stages. In the first, the new phase nucleates and grows from the supersaturated matrix. In the second stage, the supersaturation of the matrix vanishes, and a considerable quantity of energy is associated with the interface between the new phase and the matrix. In this stage, known as Ostwald ripening or coarsening, the larger precipitates are growing at the expense of the small ones and the process reaches the equilibrium state of full phase separation. Ostwald first showed that the precipitate coarsening in a solution is driven by the Gibbs-Thomson (G-T) effect.[3] The first complete analytical treatment of this growth was developed by Lifshitz and Slyozov and extended by Wanger (referred to as the LSW theory).[4] Chakraverty and Slyozov applied these concepts to treat two-dimensional problems.[5]

In this paper, it is demonstrated that concentric circle-1ike patterned structures grow on the surface of Fe/Mo multilayer systems during annealing. The surface topo-graphy was analyzed by AFM and scanning electron microscopy (SEM) after annealing the samples in high vacuum. By means of a computer simulation based on the interface thermodynamics, the development of the phase separation process was studied in surface layers of binary multilayer systems with diffusion limitation and localized coherence.

*Project supported by the Foundation of Chinese Academy of Sciences (Grant No. KJ951-A1-401) and by the International Office of the German Ministry of Education and Research.
†SHEN Dian Hong, Tel. +86-10-82649425, Fax.+86-10-82649531 E-mail: dhshen@aphy.iphy.ac.cn

Ⅱ. EXPERIMENTAL

The Fe/Mo multilayers were prepared by computer-controlled magnetron sputtering from a composite target onto a water-cooled glass substrate at an Ar pressure of 0.5Pa, after a base pressure better than 2×10^{-5}Pa had been achieved. The structure of the samples is SiO_2 (cover layer)/Fe (6nm)[Fe (6nm) Mo (2.8nm)]$_{30}$.[1] This sample consists of 30 Fe/Mo layers. The superstructure was determined by grazing-incidence X-ray diffraction. In order to study the separation of the phases in this binary system, the samples were annealed in a 1×10^{-3}Pa vacuum for two hours at temperatures between 200°C and 700°C. The samples were slowly cooled down to room temperature in the furnace. Subsequently the topography of the samples was measured by an AFM (Multi Mode, Digital Instruments) and a Scanning Electron Microscope (Hitachi). The determination of element distributions in the patterned structures was carried out by an Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF, Oxford).

Ⅲ. RESULTS

The topography measurements at these samples were taken after annealing with a scanning area of $1\mu m\times1\mu m$. It was found that the average surface roughness increases with rising annealing temperature. The results obtained from roughness analysis (R_{RMS}) of AFM height images are: 0.6, 1.8, and 2.9nm for a sample annealed at 200, 400, and 600°C, respectively.[2] This increase of the surface roughness suggests that coarsening processes were initiated by annealing. During annealing, precipitates appeared and their diameters grew with increasing annealing temperature.

AFM measurements with large scan ranges ($>60\mu m$) on the sample annealed for 2 hours at 600°C revealed some nearly concentric circular patterns (Figs.1(a) and (b)). The ana1ysis of the AFM height images showed a granular surface with small precipitates (height ≈20nm) and surrounding circular areas representing depletion zones. In some cases, large precipitates (height ≈230nm) appeared in the center of the depletion zones. The fine structures of the circular pattern may be related to the coherence of the precipitation with the lattice of the matrix.

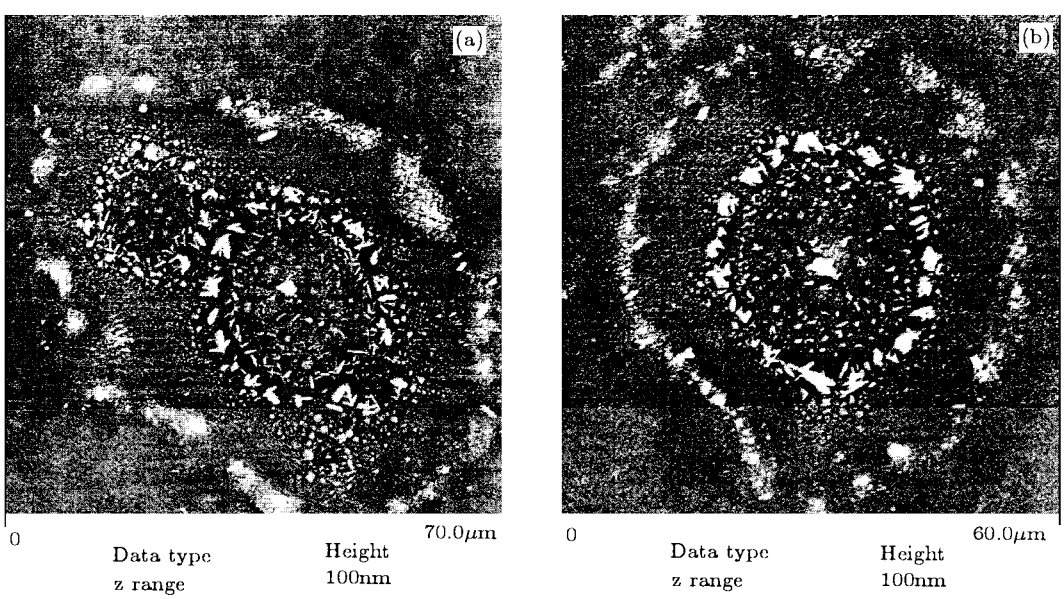


Fig.1. Atomic force microscope height images of the surface of a Fe/Mo multilayer systems annealed for 2h at 600°C, showing nearly concentric circular patterns.(a) twin concentric circular pattern, (b) single concentric circular pattern. The fine structure of the circular patterns may be a consequence of the coherence of the structures of the precipitates related to the structure of the multilayer system.

Patterns shaped similarly to those observed by AFM (Fig.1(a)) appeared in SEM micrographs (Fig.2(a)). The lateral element distribution across these patterns was measured by an EDXRF spectrometer attached to the SEM. Crossing the center of the pattern, the linear scanning profiles of elements show that the distribution of Fe is homogeneous (Fig.2(b), bottom), but the precipitates were found to be a Mo-rich phase at the ridges of the circular patterns and in the center (Fig.2(b), middle). Ostwald ripening at the

late stage of phase separation during annealing may cause such coarsening and pattern formation at the surface.

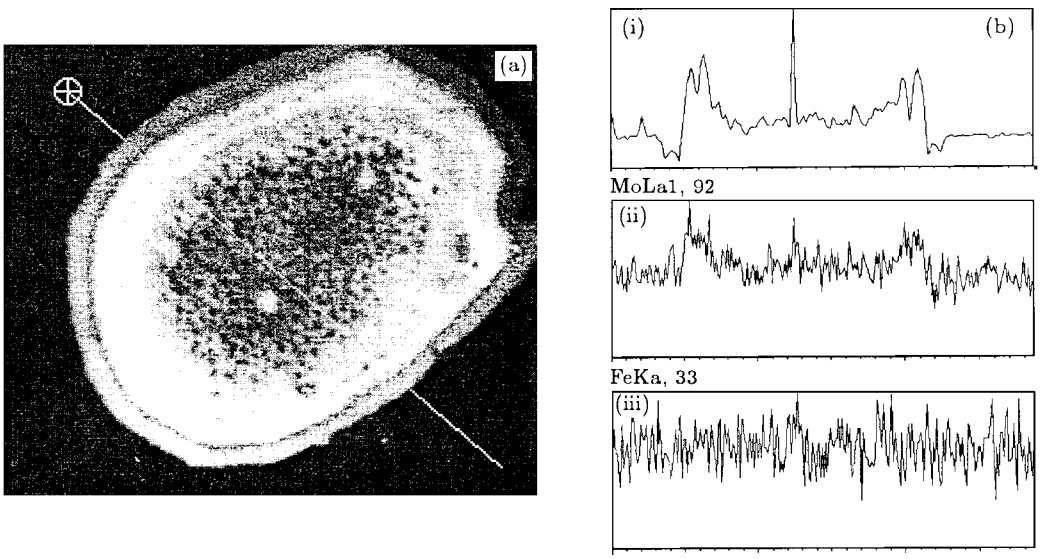


Fig.2. (a) Scanning electron microscopy micrograph of an annealed Fe/Mo multilayer system, also showing a nearly circular pattern. (b) Line profiles of the total EDXRF signal (i) and of the Fe (ii) and Mo (iii) element distribution (The profiles shown in (b) are measured along the trace marked in (a). The lenght of the linear scanning profiles is 286.4nm. The profiles shown in (b) are measured along the trace marked in (a). The length of the linear scanning profiles is 286.4nm).

IV. MODELING OF CONCENTRIC CIRCULAR PATTERN FORMATION

Based on the Gibbs-Thomson effect the coarsening of precipitation's by Ostwald ripening was modeled by computer simulations. Coarsening by Ostwald ripening is described in the literature for different multi-precipitate systems.[6,7]

The driving force for precipitate growth is the Gibbs-Thomson effect. Model calculations were performed by applying the Thomson-Freundlich (T-F) formula which was derived from the G-T relation,[8] for example, for solid solutions. The T-F formula can be linearized for any precipitate whose radius is not to small ($\geq$1nm). The T-F formula contains the first two terms of a Taylor series of the exponential term of the G-T relation is:

$$C_{\mathrm{r}} = C_{\infty}[1 + \alpha/r] \qquad (1)$$

where C_{r} is the solute concentration at the surface of a precipitate of radius r, C_{∞} denotes the solute concentration at a planar interface ($r \rightarrow \infty$), and the parameter α dependents on the specific interfacial energy, the atomic volume of the solute, and the temperature. A concentration gradient of the solute from small to large precipitates drives solute diffusion and, thus, dissolution of the small and growth of the large precipitates. The growth rate of precipitates was calculated from the diffusion equation based on the mean-field approach.

The computer program simulates a multi-precipitate system and yields the time dependence of precipitate growth based on the T-F formula and of a setting of a local diffusion limit. The computation procedure is as follows: First, a two-dimensional lattice is generated, identically sized precipitates are placed on the sites of this lattice, then a bigger precipitate is placed on the center site. The developing processes of the surrounding topography are computed using the T-F relation. A coherent length R and a critical volume ΔV are introduced. When the difference of the volume between two neighboring precipitates was larger than ΔV, the process of Ostwald coarsening started. Beyond the coherent length R, which depends on the diffusion coefficient of the solute, the competitive growth among the precipitates will stop.

Results of the above computer simulation are shown in Fig.3. They can only qualitatively explain the formation of the concentric circular patterns by Ostwald ripening because the real model parameters are not known as yet, therefore the scales of the diagrams are given in arbitrary units. The radius circular patterns are determined by the mean diffusion lengths at the surface and in the solid solution.

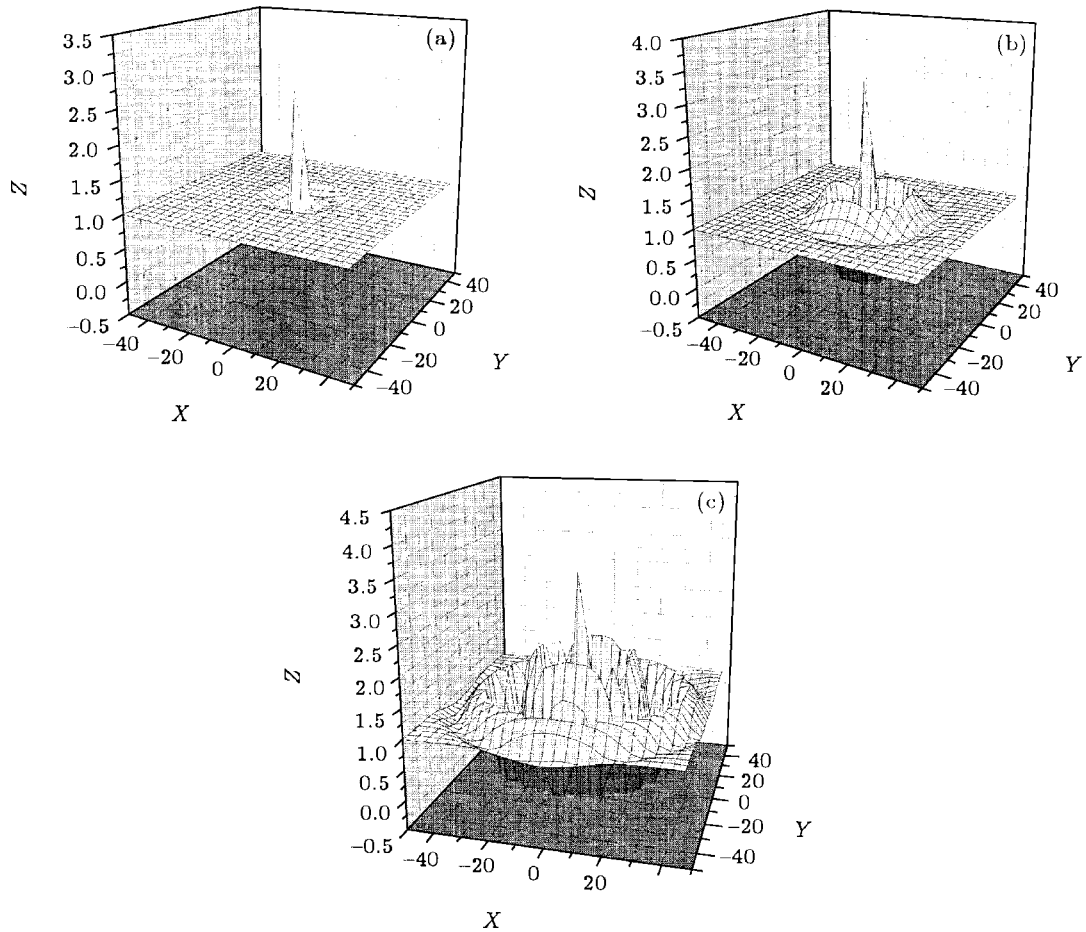


Fig.3. Evolution of circular surface patterns caused by Ostwald ripening. The patterns are obtained by computer simulations: (a) one bigger precipitate occurred on the center site, (b) and (c) visualizing the time dependence of the topography. The observation time for a, b and c is t_1, t_2 and t_3, respectively ($t_1 < t_2 < t_3$).

V. SUMMARY

The formation of concentric circular patterns of Mo-rich clusters on the surface of Fe/Mo multilayers after annealing up to 600°C at high vacuum were observed by AFM and SEM. Computer simulations support qualitatively an interpretation of the formation of circular patterns in terms of Ostwald ripening processes.

ACKNOWLEDGMENTS

The authors are thankful to Prof. Zhu Feng-wu, Beijing University of Science and Technology, for the fruitful discussion.

References

[1] Yan M L, Li S X, Yu C T, Lai W Y, Ku W J and Ge S H 1995 *Magn. Magn. Mater.* **140** 539
[2] Shen D H, Berlinger A, Nold A E, Lai E W and Luo G M 1999 *Appl. Phys.* A **68** 425
[3] Ostwald W 1900 *Z. Phys. Chem.*(Leipzig) **34** 495
[4] Lifshiz I M and Slyozov V V 1961 *J. Phys. Chem. Solids* **19** 35
Wagner C 1961 *Zeitschrift für Elektrochemie* **65** 581
[5] Chakraverty B K 1967 *J. Phys. Chem. Solids* **28** 24013
Slyozov V V 1967 *Fiz. Tverd. Tela* **9** 927
[6] Sigsbee R A 1971 *J. Appl. Phys.* **42** 3904-3915
[7] Carlow G R and Zinke-All1mang M 1997 *Phys. Rev. Lett.* **78** 460l-4604 and references therein
[8] Porter D A and Eastering K E 1981 *Phase Transformation in Metals and Alloys* (New York: Van Nostrand-Reinhold) pp 115 ff