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Observations of Fractal Patterns Induced in Thin Solid Films by Ion Irradiation

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The formation of fractal patterns during an amorphous structural transition in Ni-Mo thin films after 200-keV xenon-ion irradiation is presented. The dimension of the ion-induced fractals is 1.72 ± 0.07. The fractal patterns, together with other microscopic features, are described and characterized. Our results are compared to the cluster-diffusion-limited-aggregation model. The growth habit is attributed to long-range correlation which occurs at a critical condition during the amorphous-crystal transition.

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The current interest in fractal growth phenomena was stimulated by the diffusion-limited-aggregation (DLA) algorithm first introduced by Witten and Sander.[1] Although a variety of beautiful fractal patterns have been produced, the observations of fractal patterns from experiments are comparatively few, leading to numerous open questions concerning the essential factors which control pattern formation.[2] In this Letter, we address this issue by studying the growth of fractal patterns in ion-irradiated Ni-Mo alloy films.

In this study, ion-beam methods were employed to produce fractal patterns in thin solid films, as the methods have proved to be well suited for the study of metastable phase formation and transformation.[3,4] We present experimental observations of fractal patterns in Ni-Mo alloy films during amorphous-crystal phase transition induced by ion-beam irradiation. Possible correlations among fractal patterns, the influence of the amorphous structure, and the relationship to the critical behavior of the alloy are also discussed.

Ni-Mo multilayered films were prepared by the deposition of pure Ni and Mo alternately onto inert SiO_2 substrates in a vacuum system. The vacuum level during deposition was 5×10^{-7} Torr. The total thickness of the multilayers (about 40 nm) was designed to match the projectile range plus projectile-range straggling of the incident 200-keV xenon ions. The films consisted of three layers of Ni and two layers of Mo. The thickness of an individual layer was 7 to 10 nm. The relative thickness of the constituents was adjusted to obtain the desired alloy composition, being Ni rich for this study. The as-deposited films were then irradiated to various doses ranging from 1×10^{14} to 1×10^{16} Xe/cm^2. Irradiation was conducted at liquid-nitrogen temperature with an ion flux less than 1 μA/cm^2 to reduce the possible effects from irradiation-enhanced diffusion. The vacuum level during irradiation was better than 5×10^{-6} Torr.

The details of the experimentation can be found in our previous publications.[3,5] Rutherford backscattering, energy-dispersive spectra (EDS), x-ray diffraction, and transmission electron microscopy (TEM) were used to characterize the samples. After deposition, the overall alloy composition was determined by EDS to be $Ni_{55}Mo_{45}$.

Following doses exceeding 7×10^{14} Xe/cm^2, our Rutherford backscattering, TEM, and x-ray diffraction analysis revealed that the films were homogeneously mixed and amorphized. Lower doses induced only partial mixing, and the corresponding films are not discussed further. For doses around 7×10^{15} Xe/cm^2, a close TEM bright-field examination revealed that an atomic rearrangement took place resulting in rich microscopic features in the amorphous matrix, including islandlike structure (called cluster below), nickel-enriched precipitated phases, and fractal patterns. Two neighboring doses, i.e., 5×10^{15} and 1×10^{16} Xe/cm^2, resulted in a

homogeneous amorphous phase in both cases, indicating that doses around 7×10^{15} Xe/cm^2 correspond to a certain critical condition.

Figures 1 and 2 are typical examples of the ion-induced fractal patterns observed in the film irradiated to a dose of 7×10^{15} Xe/cm^2. The composition of these patterns was determined by EDS to be around $Ni_{50}Mo_{50}$, differing slightly from the average alloy composition of the films ($Ni_{55}Mo_{45}$). In Fig. 1, the bright-field TEM examination revealed that numerous compact clusters are distributed throughout the film, and one can also see that the fractal pattern is surrounded by a zone which is depleted in the islandlike clusters. The depletion zone was found by EDS to be molybdenum enriched. Moreover, whenever a cluster-depletion zone was present around the fractal pattern, the number density of small clusters reached its maximum at the edge of the depletion zone. By contrast, the depletion zone is not obvious in Fig. 2, and the clusters are seldom seen in the surroundings of the fractal pattern.

As the sizes of these patterns are 5–6 μm in radii, microbeam diffraction was employed to identify the structures of the observed fractal patterns. Every branch of the patterns contained several single crystals with various orientations, as the diffraction patterns changed when the analyzing beam moved from one spot to another. Diffraction patterns disappeared, however, after short exposure to the analyzing electron beam. This observation indicates that these crystals are extremely unstable.

All the ion-induced fractal patterns were quantitatively analyzed by an M-75 image-processing computer with a resolution of 512×512 pixels. The fractal dimensions were measured by our dividing the patterns into concentric disks with various radii R, and counting the occupied pixels. Occupation numbers scale as R^D, where D is the fractal dimension. Although D varied slightly from one to another, the dominant value was 1.72 ± 0.07. A remarkable characteristic is that all the patterns seem to be lopsided.

The ion-induced fractal patterns are noncentrosymmetric and have a large fractal dimension, 1.72 compared to 1.4 for the DLA model, indicating that the patterns are quite different from those produced by computer simulation based on the DLA model. The observed patterns look similar in some aspects to those stimulated by the cluster-diffusion-limited-aggregation (CDLA) model,[6] which is a generalization of single-particle DLA. For instance, both the measured fractal dimension and the depletion zone are consistent with the CDLA model. According to the CDLA model, growth begins by the occupation of a fraction of the available sites and the positioning of a seed at the origin. The occupied sites are visualized as particles that remain fixed, while the growing clusters undergo a random walk gathering up the fixed particles. Unfortunately, however, the driving force for cluster motion has not been identified, and so mapping the observed patterns onto the CDLA model is still questionable. The process of the formation of ion-induced fractal patterns in thin solid films seems likely to involve some stationary large clusters and the motion of small species. Besides, long-range correlation is prob-

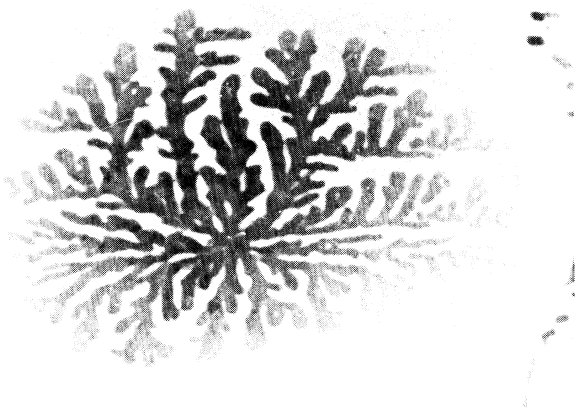

FIG. 1. Fractal pattern formed in $Ni_{55}Mo_{45}$ metal layers after ion mixing to a dose of 7×10^{15} Xe/cm^2. The matrix is amorphous; the small dark dots are what we call "clusters." The needlelike structures are precipitates of Ni-enriched phase.

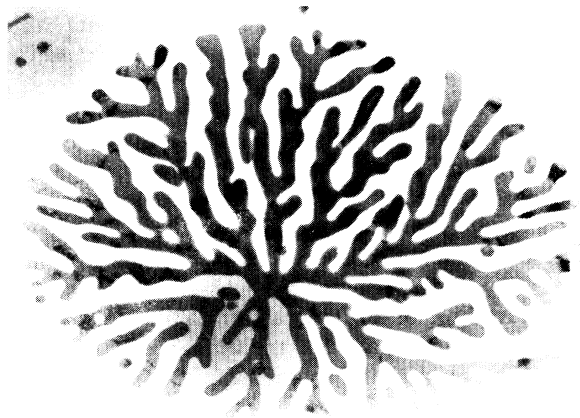

FIG. 2. Fractal pattern formed in the same sample as Fig. 1. Clusters are seldom seen. The difference in appearance is addressed in the paper.

ably necessary for the formation of fractals in amorphous films. Overall, this issue needs still more studies both experimentally and theoretically.

As mentioned above, the fractal patterns were primarily composed of 1-μm single crystals, permitting composition analysis by EDS. The composition was around $Ni_{50}Mo_{50}$. This composition corresponds just to the δ phase in the Ni-Mo equilibrium phase diagram. The Ni-Mo δ phase, however, has a very complicated orthorhombic structure with 56 atoms in a unit cell forming a specific ordering configuration.[7] To crystallize such a sophisticated structure obviously requires higher temperatures and longer times than required for simple structures. Since these conditions are not met in our ion-irradiation experiments, these single crystals could not be the δ phase. The instability of the crystals under analyzing electron-beam irradiation also excludes the δ phase, since the δ phase is very stable. This conclusion is also supported by the fact that room-temperature ion mixing of $Ni_{50}Mo_{50}$ multilayers resulted in an amorphous phase, whereas the recrystallization temperature for the δ phase is over 600 °C.[8]

After exposure to the electron beam, the fractal patterns retained their shape, but the crystals transformed to the amorphous state as observed by high-resolution TEM. This structural change is similar to the observations by one of the authors[9] that a metastable crystalline Ni-Mo phase of hcp structure transformed into amorphous structure upon room-temperature aging.

It should be noted that the fractal patterns are frequently observed in an amorphous background. The amorphous structure therefore apparently plays an important role in the formation of the fractal patterns.

Ben-Jacob *et al.*[10] proposed that the dense branching morphology is generated in an amorphous annealing experiment. The reason why other kinds of patterns could not grow was thought to be due to the difference of the microscopic structures of the matrix. In our experiments, an amorphous matrix was also necessary for the fractal patterns to grow. This conclusion is based on the observations mentioned above as well as on the fact that at lower dose, when the films remained crystalline, nonfractal dendritic patterns were formed.[11] We therefore believe that the fractal patterns observed are due to a specific growth mode being excited in the isotropic amorphous matrix. The excitation idea was also proposed by Orbach[12] on the basis of his experimental results that fractal excitation could be achieved in an amorphous material.

As mentioned above, TEM examinations revealed that the amorphous films underwent an atomic rearrangement only under restricted conditions, namely after irradiation to the dose around 7×10^{15} Xe/cm^2, while in two other films irradiated to a little bit lower and higher doses, i.e., 5×10^{15} and 1×10^{16} Xe/cm^2, respectively, no fractal pattern but a homogeneous amorphous phase was observed. These indicate that the fractal patterns were formed at a critical condition during the amorphous structural phase transition. The amorphous phase transition, though not ideal, is a second-order phase transformation.[13] At such a transformation, long-range correlations are present and such correlations[14] would surely have a great influence on pattern formation. As Goldstein suggested in his approach to the relaxation behavior of the glass transition, these critical fluctuations would cause cluster motion.[15] In this study, TEM examination indeed revealed the islandlike clusters.

We conclude by stressing that our experiments show some correlations existing between the fractal patterns and the amorphous structural phase transformation. Our work also demonstrates the great potential of ion-beam methods for the investigation of pattern formation.

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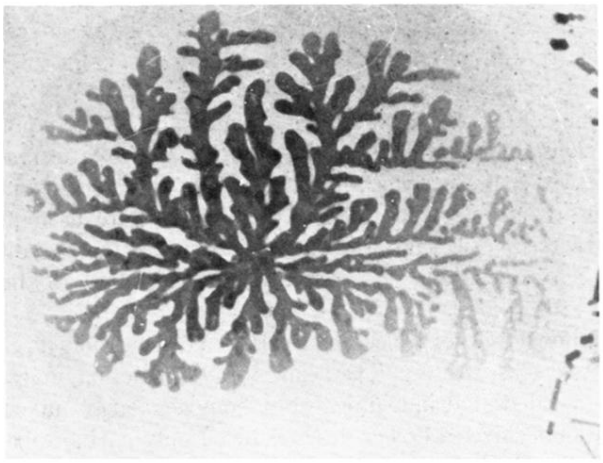

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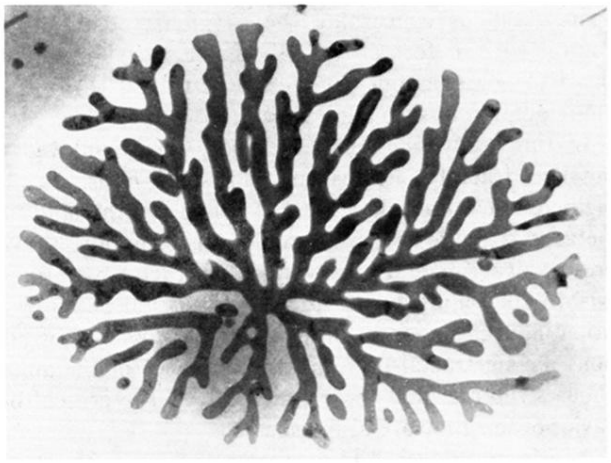

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