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LETTER TO THE EDITOR

Nucleation–aggregation of molybdena crystals at the vapour–solid interface

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Abstract. The analysis of scanning electron microscopy (SEM) for molybdena fractal clusters produced during the gas–solid phase transition reveals the relationship between the microstructure and macroscopic morphology in the development of interfacial patterns. The clusters demonstrate two structural forms: stack-like formation and network formation. Each pattern displays a microscopical crystallographic anisotropy although they are macroscopically self-similar. A nucleation–aggregation (NA) model is suggested to explain the non-equilibrium growth processes.

Many natural systems produce fractal patterns that display 'dilation symmetry' [1]. They look geometrically self-similar under transformation of scale such as changing the magnification of a microscope. Some successful experimental studies have been reported previously, such as the electrochemical deposition of zinc-metal leaves [2–4], the dielectric breakdown [5], the sputter-deposited Nb–Ge alloy film [6] and the fractal growth in Ni–Mo alloy film [7, 8].

Several models of kinetic growth have been suggested in order to interpret the chemical and physical growth process occurring in the precursor phases. Examples of these models are the diffusion-limited aggregation (DLA) model, the diffusion-limited cluster aggregation (DLCA) model and the modified random-rain (RR) model [9–11].

In this paper, I report an experimental study of a molybdena fractal cluster. Many fractal patterns and ribbon-like crystals are formed on the smooth surface of alumina substrate after properly heating molybdena powder in a mixture of argon and oxygen gases. These patterns are characterized by the random tree-branch structures, seem to have no natural length scale and thus exhibit scale invariance.

The experimental set-up that has been chosen for this study is a vapour-deposition system. The high-purity molybdena powder was used as the source material. After evacuating, the system was first filled with dry argon to 152 mm mercury absolute pressure and then refilled with dry oxygen up to 760 mm Hg. The temperature was selected between 750 and 850 °C, and the duration ranged from 0.5 to 2 h.

The system was program-cooled from the temperature selected to 400 °C at a rate of 2 °C per minute, and from 400 °C to room temperature at 5 °C min⁻¹. Details of the experimental process can be found elsewhere [12].

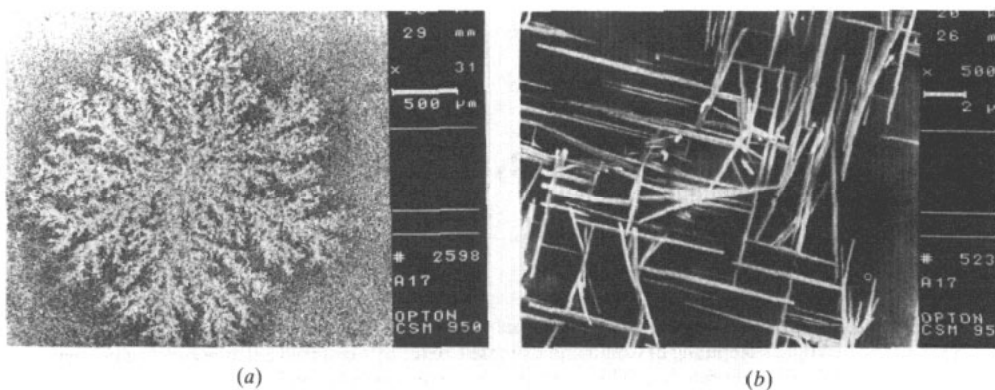


Figure 1. The cluster of whiskers featured by the stack-up, at two different magnifications. ($T = 750^{\circ}\text{C}$, $t = 0.5\text{ h}$): (a) the morphology of the fractal structure; (b) the closer view of the cluster.

Analysis of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out for the fractal structures and ribbon-like crystals, respectively. Rutherford backscattering spectrometry (RBS) and the x-ray diffraction (XRD) technique were also employed to determine the thickness and structure of the molybdena crystal. The fractal dimension measurement was performed by a model-75 computer of the International Imaging System.

Figure 1 shows the SEM images of a fractal cluster grown at 750°C for 0.5 h. Figure 1(a) demonstrates a highly ramified cluster of molybdena crystals. Figure 1(b) is a closer view of the fractal cluster at a magnification of five thousand. It is clear from figure 1(b) that each branch of the fractal cluster consists of many needle-like whiskers. These whiskers have the same shape, with a length in the range of 2 to $9\text{ }\mu\text{m}$, and a width of 600 to $30\,000\text{ \AA}$. It is significant that most of these whiskers stacked together in parallel or perpendicularly.

The micrographs of another molybdena fractal pattern grown at 800°C for 2 h are shown in figure 2. Figure 2(a) shows a network fractal pattern that is quite different from the one shown in figure 1(a). Figure 2(b) is a closer view of the fractal pattern at a magnification of two thousand. The most noteworthy feature from figure 2(b) is that this fractal pattern consists of many bunched palm-like formations along with numerous cuboid-like crystals dispersed uniformly on the whole pattern. The palm-like formations linked the neighbouring ones and produced an odd-looking and intricate vine—the branch of the network pattern. The dimensions of the cuboid-like crystals are about 2– $10\text{ }\mu\text{m}$ in length, 2– $8\text{ }\mu\text{m}$ in width. Figure 3 is the SEM photograph of tip-splitting pattern of molybdena cluster grown at 825°C for 1 h. The splitting structure consists of many molybdena crystals that stack together in parallel. These crystals are narrow and thin. The dimensions of the tip-splitting structure is about $10\text{ }\mu\text{m}$. Several smaller clusters are deposited in the region of the splitting structures.

One of the patterns computer-generated by the nucleation-aggregation (NA) model is shown as figure 4. This NA model is suggested in an attempt to explain the observation of fractal clusters grown at the vapour–solid interface. The model is simulated on a computer by starting with a seed at a particular site. The seeds have been observed experimentally, consist of some tiny crystals or whiskers and some have an asterisk shape

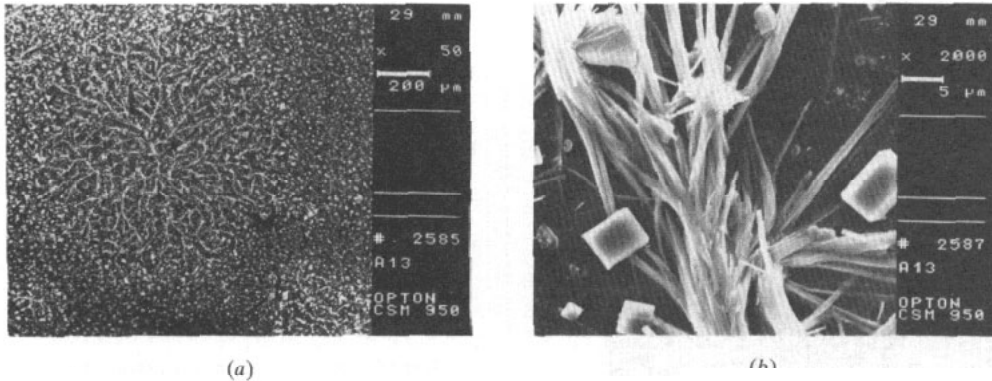


Figure 2. The palm-like structure formed by the bunchy crystals and cuboid-like crystals. ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$): (a) the pattern magnified fifty times; (b) the closer view at magnification of two thousand.

[12]. In the second stage, a large number of short lines (representing the whiskers) move as a unit, randomly. A growth event occurs when a random short line lands on a site neighbouring the seed, thereby increasing the seed size.

The major difference between the NA model and DLCA model is that it allows the short line to deposit randomly on the whole growing pattern including its interior. It is similar to the RR model from the point of view of random deposition [11].

The result of this process is a self-similar dense object with an obvious centre (see figure 4). The pattern obtained using the NA model corresponds to the fractal cluster shown in figure 1(a). The NA model should therefore give rise to aggregates with high fractal dimension. The fractal dimension of a more compact structure is measurably larger than that predicted by the DLA model in two dimensions ($D = 1.67$). Heating at $750\text{ }^{\circ}\text{C}$ leads to the stack-like formation whose fractal dimension is $D = 1.96$, and heating at $800\text{ }^{\circ}\text{C}$ gives the network structure with $D = 1.89$.

Figure 5 is one of the TEM micrographs of a molybdena ribbon crystal grown at $850\text{ }^{\circ}\text{C}$ for 1.5 h. The thickness of the crystal is 3350 \AA measured by RBS. The TEM analysis was

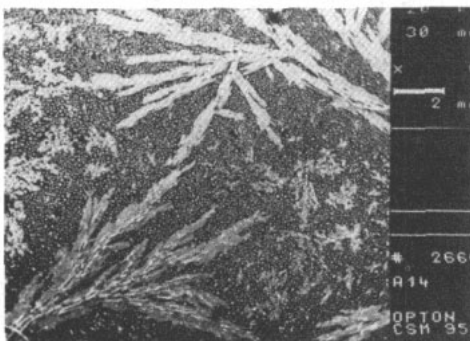


Figure 3. The tip-splitting pattern of molybdena crystal cluster grown at $825\text{ }^{\circ}\text{C}$ for 1 h.

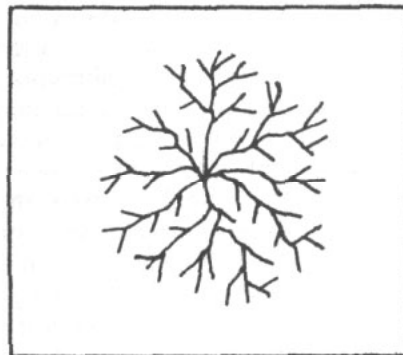


Figure 4. One of the patterns. NA model computer-generated.

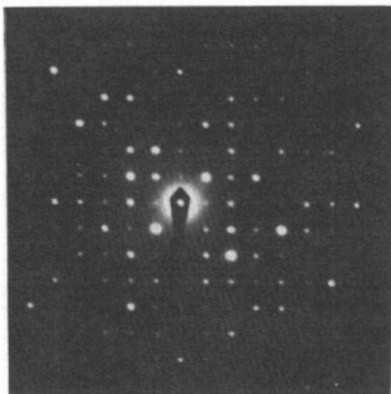


Figure 5. TEM micrograph of a vapour-deposited molybdena ribbon crystal.

carried out by JEM-1000. The calculation result shows that the crystal belongs to the orthorhombic system with the lattice constants $a = 3.97$ $b = 13.87$ $c = 3.70$. The result of Laue x-ray front reflection pointed out that the ribbon crystal is a single crystal.

It is pointed out in figures 1 and 3 that the growth process of each fractal pattern may involve two consecutive stages, i.e., crystallization and diffusional clustering. The growth process may be as follows.

When a molybdena powder in the experimental set-up was heated, it started to evaporate and diffuse through the whole space of the system. There should be a concentration gradient of molybdena molecules. As soon as the molybdena molecules in vapour phase reached the critical concentration, they nucleated and formed crystals (needle-like whiskers, ribbon-like crystals, or palm-like ones). Because the fluctuation of the temperature and concentration over the whole space of the system existed at all times, the spatial correlation took place at a certain critical point, and some 'seeds' of fractal pattern were then formed on the gas–solid interface. For the second stage, the whiskers or ribbon-like crystals aggregated according to their seed's shape. With increased time, the seed of each fractal pattern grew continuously by a subsequent stacking process. These fractal structures make a feature of stack-like formation as shown in figures 1 and 3.

The crystalline structure of molybdena grown by vapour deposition is orthorhombic, and the [001] crystallographic direction is the preferable growth direction as compared with other directions. It is for this reason that the whiskers and ribbon-like crystals are easy to grow. The whiskers or ribbon-like crystals prefer to stack together in parallel or perpendicularly in order to decrease their surface free energy.

With respect to the fractal pattern shown in figure 2, it is assumed that there may be a special dominant factor controlling its growth process. The molybdena molecules in the vapour phase crystallize easily, their crystal growth occurring following widely different modes, and form a wide variety of crystals during the gas–solid phase transition. The odd-looking and intricate vines shown in figure 2 are one example. An interesting phenomenon is that these odd-looking vines grew continuously and finally formed a network fractal pattern. This is a kind of continuous-growth mode. The extra molybdena molecules in the vapour phase nucleated simultaneously, and crystallized out the cuboid-like crystals.

It is worth noting that the patterns shown in figures 1–3 are self-similar macro-

scopically but they display microscopical anisotropy. That means the whiskers or crystals belong to an ordered growth under microscopical equilibrium, and they form a disordered fractal structure under macroscopical non-equilibrium conditions during the irreversible two-dimensional growth.

The fractal clusters can be reproduced experimentally, but the random fractal patterns differ from each other, and exact identical patterns were never obtained. The experimental conditions must be controlled carefully during the experiment period, otherwise no fractal pattern can be produced.

In summary, the NA model can be used to interpret the growth process of a molybdena fractal cluster. The stack-like fractal clusters shown in figures 1 and 3 belong in an ensemble of similarly produced needle-like whiskers or ribbon-like crystals. On the other hand, the single diffusing whisker or crystal aggregates onto a growing cluster. In the case of the network fractal growth, the fractal pattern shown in figure 2 is an aggregate of the fascicular crystal vines. It is significant that the crystallographic anisotropy manifests a fractal feature macroscopically. Moreover, these real aggregates in this work imply that the formation of molybdena fractal patterns far from equilibrium is a self-organized critical phenomenon occurring in its phase transition. The information obtained so far paves the way for further experiment to determine the details of the physical mechanism responsible for the structures.

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