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Morphology of molybdena fractal clusters grown by vapour-phase deposition

JI-ZHONG ZHANG
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084 and Center of Condensed Matter and Radiation Physics, CCAST (World Laboratory) PO Box 8730, Beijing, People's Republic of China

DELU LIU
Department of Materials Physics, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

Molybdena fractal clusters of various shapes were obtained experimentally in an evaporation-deposition system. The open ramified deposits grew after heating MoO_3 powder at 750–900 °C for 0.5–2 h. They demonstrate two structural forms: the stack-like formation and the net-like one. Scanning electron microscopy observations revealed that the clusters consist of one of three different microstructures: needle-like whiskers, ribbon-like crystals, and fascicular crystals. Each pattern displays the microscopical anisotropy although they are of macroscopical self-similar feature. A nucleation-aggregation model is suggested to explain the non-equilibrium growth processes.

1. Introduction

It has been well known that fractal geometry is a natural concept used to describe random or disordered objects ranging from branched polymers to the earth's surface [1]. It has emerged as an essential idea for understanding the kinetic growth of disordered materials. Disordered materials often display dilation symmetry, which means they look geometrically self-similar under transformation of scale, such as changing the magnification of a microscope. Fractal structures are often observed in an irreversible non-equilibrium growth process.

Several real experimental systems have been reported previously, for example, the fractal aggregation in Ni–Mo alloy films induced by ion implantation, the fractal corrosion of alloy films by acid, the fractal structures of zinc–metal leaves grown by electrodeposition, the fractal aggregates in sputter-deposited $NbGe_2$ films, and the two dimensional silica colloidal aggregates at an air water interface, etc. [2–7]. Some of fractal aggregates take place at an appropriate interface during phase transition.

Various models of kinetic growth have been suggested, such as the reaction-limited aggregation, the gas phase one (ballistic growth), and the diffusion-limited one [8–10]. A number of computer generated structures which result from simple rules (typically governing mass transport and accretion) are also reported [11–13].

We report an experimental study of the irreversible two dimensional growth of molybdena fractal cluster. Many fractal patterns grew on an alumina plate surface after properly heating molybdenum sheet or molybdena powder in a mixture of argon and oxygen gases. These patterns are characterized by the open, random, and chain-like structures, seem to have no natural length scale and thus exhibit scale invariance.

2. Experimental procedure

The experimental set-up used here for investigating molybdena fractal growth is an evaporation-deposition system. The molybdenum metal sheet of 0.2 mm thickness or high purity molybdena (MoO_3) 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 900 °C, and duration from 0.5 to 2 h.

The system was program-cooled from the temperature selected to 400 °C at a rate of $2\,^{\circ}\mathrm{C\,min^{-1}}$, and from 400 °C to room temperature at a rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$. Various fractal clusters along with some long strip-like crystals, and cuboid ones under certain conditions, were found on the alumina substrate surface. The details of the experimental process can be found elsewhere [14].

3. Results and discussion

The scanning electron microscopy (SEM) images of the fractal cluster grown at 750 °C for 0.5 h shown in Fig. 1a demonstrates a highly ramified branched cluster of molybdena crystals. Fig. 1b is a closer view of the fractal cluster at a magnification of 5000. It is clear from Fig. 1b that each branch of the fractal cluster

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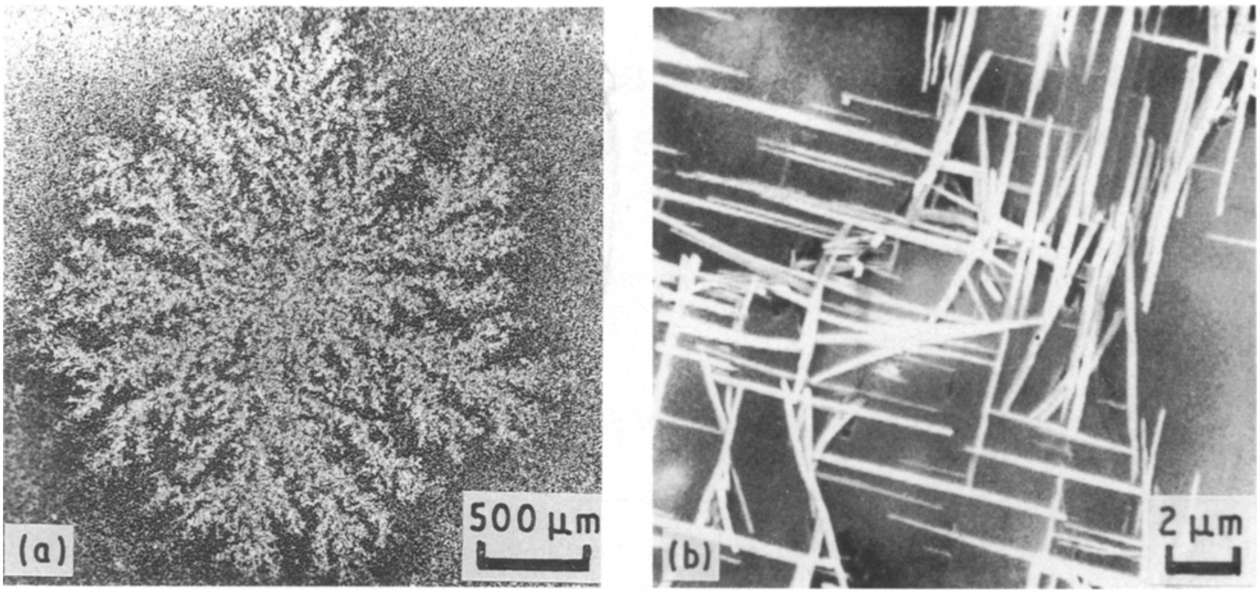

Figure 1 SEM images of a typical stack-like fractal cluster grown at 750 °C for 0.5 h: (a) general view and (b) closer view of the cluster.

consists of many needle-like whiskers. These whiskers have the same shape, with a length in the range of 2–12 µm, and a width in the range of 60–350 nm. It is significant that most of these whiskers stacked together parallelly.

Fig. 2a and b are the micrographs of another fractal pattern of molybdena crystals grown at 800 °C for 2 h. Fig. 2a shows a net-like fractal pattern which is quite different from one shown in Fig. 1a. A closer view of the fractal pattern at magnification of 1000 is given in Fig. 2b. It is the most noteworthy feature of Fig. 2b that this fractal pattern consists of many bunchy palm-like formations along with many cuboid-like crystals dispersed uniformly on the whole pattern. Each palm-like formation linked with its adjacent one and formed an odd-looking, intricate vine – the branch of the net-like random pattern. The dimensions of the cuboid-like crystals are about 2–10 µm in length, 2–8 µm in width.

The micrograph of the fractal cluster grown at 900 °C for 2 h in Fig. 3a shows a ramified cluster of molybdena crystals, and it appears to be roughly fractal deposit. Fig. 3b is a closer view of the fractal pattern. It is seen clearly from Fig. 3b that many ribbon-like crystals, stacked parallelly, form each branch of the pattern. All of the ribbon-like crystals have the same narrow strip-like shape with both ends flat, with a length in the range of 100–250 µm, and a width in the range of 2–20 µm. The size of this pattern is up to approximately 1.5 cm.

Fig. 4 shows an interesting experimental result. Two different kinds of patterns were obtained simultaneously after heating molybdena powder at 750 °C for 2 h. The pattern on the left is obviously a stack-like cluster, and the right one is a net-like formation. It is revealed from Fig. 4 that the stack-like fractal cluster and the net-like one can be formed under the same experimental conditions.

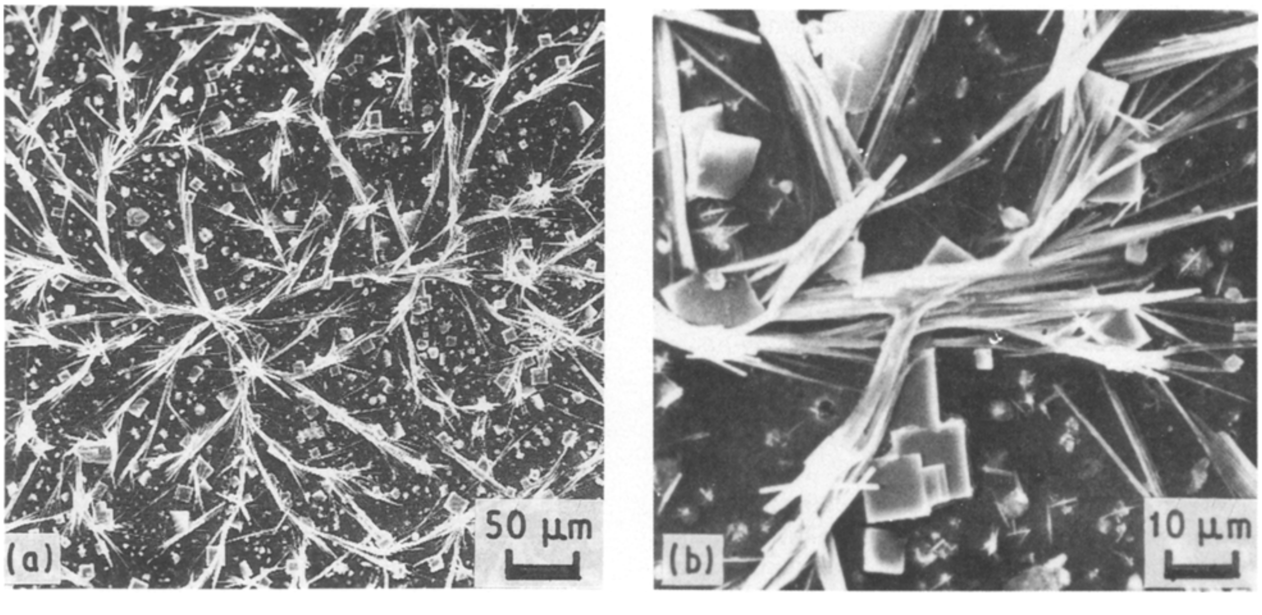

Figure 2 Micrographs of the net-like fractal pattern grown at 800 °C for 2 h: (a) general view and (b) closer view of the pattern.

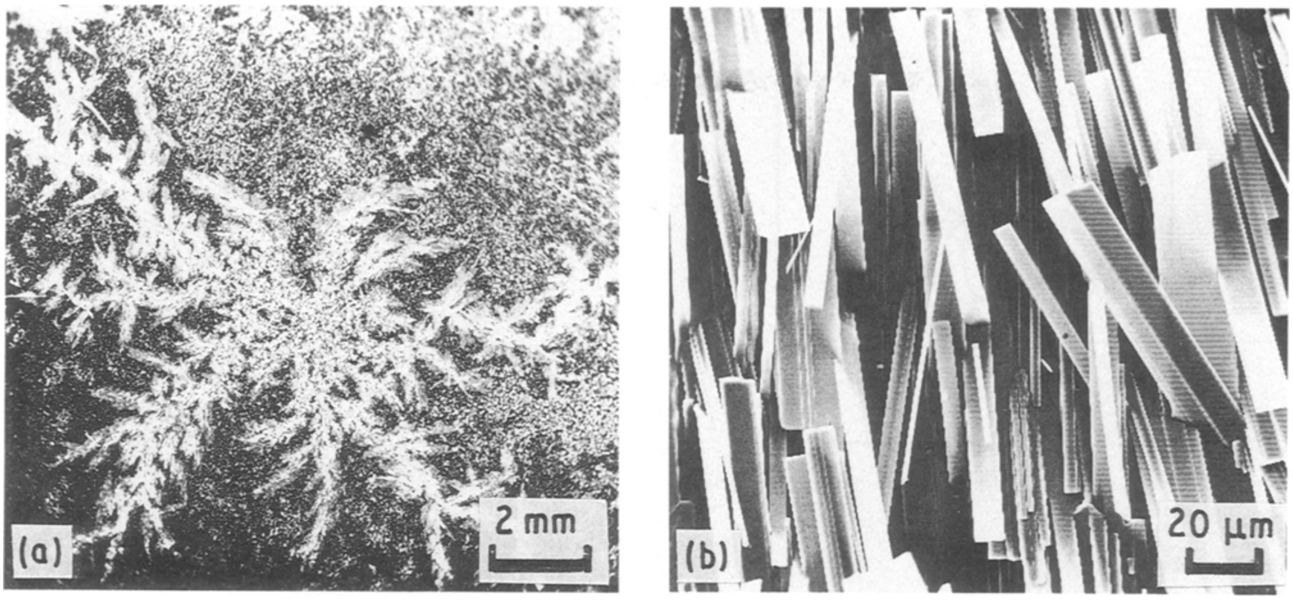

Figure 3 SEM photographs of another stack-like fractal cluster grown at 900 °C for 2 h: (a) general view and (b) closer view of the cluster.

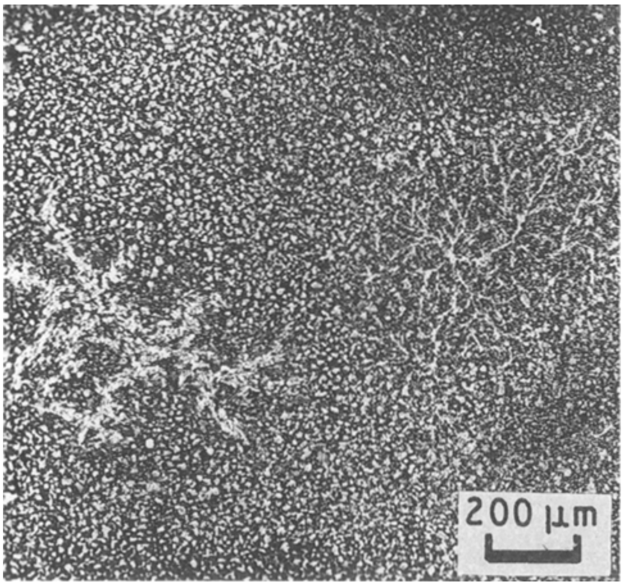

Figure 4 Micro-image of coexisted net-like fractal pattern and stack-like one grown at 750 °C for 2 h.

It is pointed out from Figs 1–3 that the growth process of each fractal pattern may involve two consecutive stages, i.e., crystallization and aggregation. The growth process may be as follows.

When the molybdena powder in the experimental set-up was heated, it started to evaporate and diffuse to 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 a critical concentration, some crystals (needle-like, bunchy, or ribbon-like crystals) then nucleated and formed. Because the fluctuation of temperature and concentration over the whole space of the system always existed, the spatial correlation took place at certain critical point, and some seeds of fractal pattern then formed. For the second stage, the needle-like crystals or ribbon-like ones 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 Figs 1 and 3. The bunchy crystals grew up continuously until they met an adjacent one, and then grew again (diffusional clustering) at the outer portion of the pattern. The final structure formed by the bunchy crystals is characteristic of net-like formation as shown in Fig. 2. The extra molybdena molecules in the vapour phase nucleated simultaneously, and crystallized out the cuboid-like crystals.

The saturated vapour pressure of the molybdena (MoO_3) is more than 1 mm Hg absolute pressure at 750 °C. The saturated vapour pressure increases quickly at high temperature. The concentration of molybdena molecules in the system at 900 °C is about 30 times greater than that at 750 °C [15]. The size of the ribbon-like crystals in Fig. 3 is much larger than one of the needle-like whiskers in Fig. 1 because of higher concentration and larger growth rate.

The growth processes as stated above are a feature of nucleation, and can be considered as a two dimensional nucleation-aggregation (NA) model. These fractal clusters may be of different crystalline morphology or even lattice, for example, the whiskers, ribbons or fascicular crystals, but the nucleation is an essential dominant factor determining their growth processes. A computer program has been used to simulate the growth process by NA model. Fig. 5 is one of the results obtained by the computer simulation. It is in good agreement with the pattern shown in Fig. 1a.

The scale invariance is tested by calculating the density–density correlation function for the digitized patterns of the micrographs. the fractal dimension of these molybdena clusters is 1.96, 1.89, and 1.83 corresponding to the fractal patterns shown in Figs 1–3.

The three dimensional structure of sphene crystals produced in a soda-lime–alumina–titania–silica glass specimen by heating at 800 °C for 1 h gives more evidence for the NA model. Its cross-section pattern is shown in Fig. 6. The pattern is an open, random,

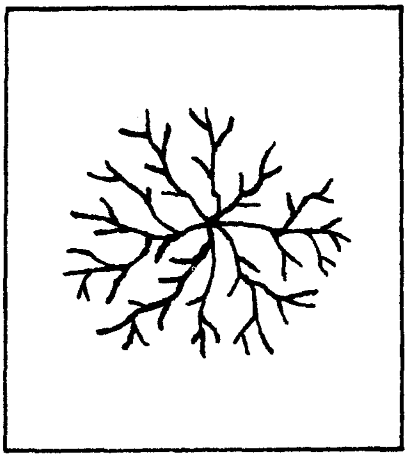

Figure 5 One of the computer-generated patterns by the nucleation-aggregation model.

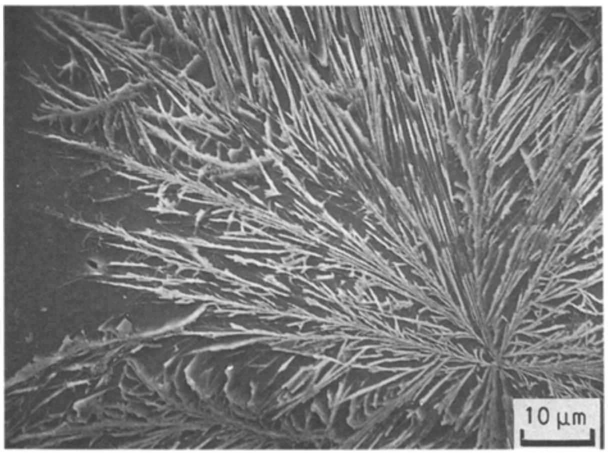

Figure 6 Fractal structure of sphene crystals produced in a soda-lime–alumina–titania–silica glass specimen during heating at 800 °C.

ramified structure. Its growth process could well be explained by the NA model. The difference between the molybdena fractal clusters and sphene crystal fractal structures is the dimensionality, that is, two dimensional for the molybdena clusters and three dimensional for sphene crystal structures.

4. Conclusion

The fluctuation of temperature and MoO_3 concentration may be quite different at each possible growth site. The seed of each fractal pattern was also of different shape and structure. As soon as a seed was formed, the microstructure of the final fractal pattern will depend only on the seed's structure. Many interfacial fractal patterns of molybdena crystals, which were often accompanied by some long strip-like crystals and cuboid ones, have been observed by vapour-phase deposition in the experimental set-up. The experimental results can be reproduced, 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 experimental period, otherwise no fractal pattern can be produced. The evaporation-deposition method offers a very attractive way to study fractal growth of some oxides.

In summary, the stack-like and net-like fractal clusters shown in Figs 1–3 belong in an ensemble of similarly produced needle-like whiskers or ribbon-like crystals or bunchy ones. On the other hand, the single diffusing whiskers, or ribbon-like crystals, or bunchy crystals aggregate on to a growing cluster. The fractal pattern shown in Fig. 2 is an aggregate of the fascicular crystal vines. It is significant that the crystalline anisotropy manifests macroscopically a fractal feature. The information obtained so far, points the way towards further experiment to determine the details of the physical mechanism responsible for the structures.

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