Structural characteristics of fractal clusters grown during vapor-solid transformation

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Fractal growth of molybdena, iodine, and carbon during vapor-solid transformation was studied experimentally. Three types of self-similar fractal clusters were observed, respectively. These clusters included two different crystalline structures, that is, single crystal and amorphous solid. The microstructure of single crystals included whiskers, ribbonlike crystals, and dendrites. The whiskers or ribbonlike crystals stacked together easily, and formed a bifurcation aggregate such as a molybdena fractal cluster. Under certain conditions, some dendrites were distorted and became branches of a network cluster, such as an iodine quasifractal cluster. The branching amorphous clusters of carbon aggregated at the edge of a glass sample after being irradiated by an electron beam. It is revealed phenomenologically from the experimental results that microstructures of these fractal clusters depended strongly on their growth conditions. [S1063-651X(97)13505-X]

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I. INTRODUCTION

Self-similar or self-affine fractal structures with features similar to fractal models reported earlier [1] can be found in nature on all astronomic as well as microscopic length scales. Examples include clusters of galaxies [2], the distribution of earthquakes, and the structures of coastlines, rivers, and clouds [3]. Fractal cracks occur on length scales ranging from 1000 km (such as the San Andress fault) to micrometers (like fractures in solid materials) [4]. The fractal concept has become an important tool for understanding irregular complex systems in various scientific disciplines [5–10]. Many theoretical and experimental studies have been carried out in the past 20 years. A number of complicated and fascinating fractal patterns were obtained by computer simulation or experiments. It is very important to explain the growth process of these fractal patterns. The interplay between the macroscopic driving force associated with the phase transformation and microscopic interfacial dynamics is one of the most challenging topics.

Study on crystal growth under nonequilibrium conditions is helpful to understand the above question. In general, this kind of crystal growth can result in various complex patterns that are similar to those found in processes such as viscous fingering, aggregation, and electrochemical deposition. Most of the research has been focused on systems in which the macroscopic dynamics is determined by a diffusion field. For such systems, the patterns that form spontaneously may be grouped into a small number of typical ''essential shapes'' or morphologies, observed in different systems and over many length scales [11].

In this paper the fractal growth of molybdena, iodine, and carbon during vapor-solid transformation is reported. These interfacial fractal clusters consist of whiskers, single crystals, dendrites, and amorphous clusters, respectively, and reveal phenomenologically different growth kinetics that depends upon the corresponding growth condition.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Stacking fractal of molybdena crystal

Self-similar two-dimensional fractal clusters of molybdena were observed during vapor-solid transformation. The experimental setup that has been chosen for this study is a vapor-deposition system. The high-purity molybdena powder was used as the source material. The temperature was selected between 750 and 900 °C, and the duration ranged from 0.5 to 2 h. The system was program-cooled from the selected temperature to 400 °C at a rate of 2 °C per minute, and from 400 °C to room temperature at 5 °C per minute.

Figure 1(a) shows the scanning electron microscopy (SEM) image of a fractal cluster grown at 750 °C for 0.5 h. This is a highly ramified cluster of molybdena crystals. Figure 1(b) is a closer view of the fractal cluster at a magnification of 5000. It is clear from Fig. 1(b) that each branch of the fractal cluster consists of many needlelike whiskers. These whiskers have the same shape, with a length in the range of 2–9 μm, and a width of 60–300 nm. It is significant that most of these whiskers stacked together in parallel or perpendicularly. This kind of fractal cluster is characteristic of stacking, and may be called a ''stacking fractal.'' The stacking fractal is totally different from other fractal aggregates reported earlier [12–14].

The micrograph of a molybdena fractal cluster grown at 900 °C for 2 h shows another kind of stacking fractal. Many ribbonlike crystals stacked in parallel formed each branch of the cluster as shown in Figs. 1(c) and 1(d). All of the ribbonlike crystals have the same narrow striplike 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.

A nucleation-aggregation (NA) model is proposed to explain the stacking fractal of molybdena single crystals [15]. The NA model allows the whiskers or ribbonlike crystals to deposit randomly on the whole growing pattern including its interior. It is similar to the random rain (RR) model from the

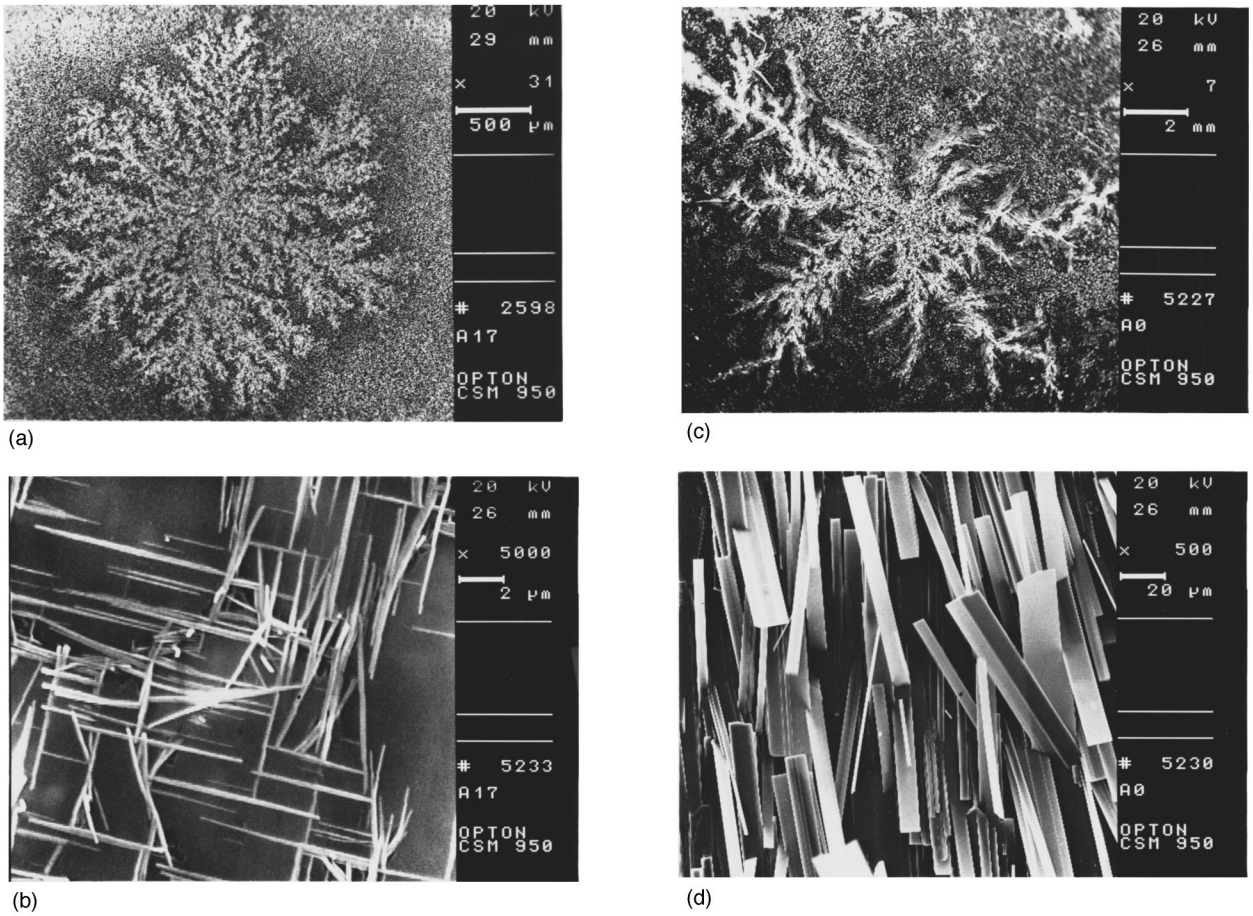


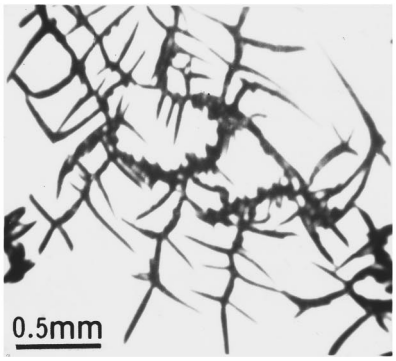
FIG. 1. (a) The cluster of molybdena whiskers featured by the stackup, grown at 750 °C for 0.5 h. (b) The closer view of the cluster shown in (a). (c) The cluster of molybdena ribbonlike crystals featured by the stackup, grown at 900 °C for 2 h. (d) The closer view of the cluster shown in (c).

point of view of random deposition [16]. The major difference between the NA model and the DLA (diffusion limited aggregation) model [17] is that the growth rate of the fractal cluster is controlled by a stacking process rather than a diffusion process. The stacking fractal of molybdena crystals was formed due to temperature field, concentration fluctuation, and long-range correlations of molybdena molecules in the system out of equilibrium. The experimental temperature had considerable effect on the stacking form and morphology of the fractal cluster.

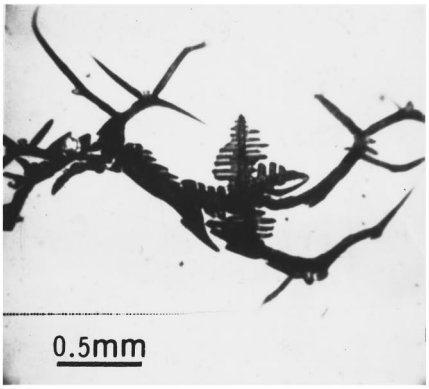
B. Quasifractal structure of iodine dendrite

Fractal aggregation of iodine during vapor deposition was also studied experimentally. A set of glass equipment was employed for this work. The commercial iodine crystal was used as the source material, and heated by an electrical heater. The temperature was selected between 110 and 140 °C. The iodine vapor evaporated from the iodine source was cooled at a different cooling rate that ranged from 0.6 to 2 °C per second. The iodine vapor deposited on a piece of pentaerythrite (PET) film covered the inner wall of the glass container. A wide variety of iodine deposits was obtained on the surface of the PET film.

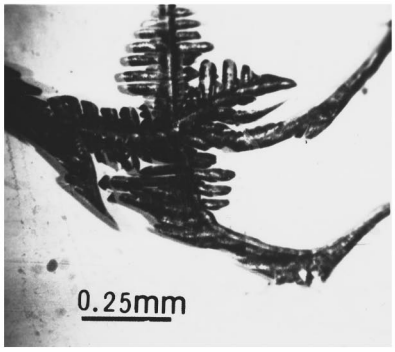
The iodine deposits displayed mostly three different morphologies: the fractal cluster, quasifractal network cluster, and sixfold symmetrical snowflakelike crystals. The self-similar fractal cluster (not shown here) consisted of many globular chains. The diameter of the globule is between 20 and 110 μm. A quasifractal network cluster of iodine deposits grown at 130 °C for 1.5 min is shown in Fig. 2. It is clear from Fig. 2(a) that this network cluster consisted of numerous branch crystals, and is a complicated structure between the standard fractal cluster and symmetrical dendrite. Figure 2(b) is particularly significant in an understanding of the morphology transition. There exists a network pattern containing several dendrites. It can be seen from Fig. 2(b) that some side branches of the dendrites were distorted (that is, a major modification of the dendrite's shape) during their growth process, and grew up more easily than the others and became the constituent part of the network cluster. It is revealed that these dendrites were strongly influenced by certain perturbation during their growth process. Some side branches of the dendrites were affected by long-range correlations, and changed their morphologies. The closer view of the distorted dendrites is shown in Fig. 2(c). The dominant factors that affect the growth process of a quasifractal network cluster are considered to be the same as those in the molybdena case mentioned above. The quasifractal network cluster and distortional dendrites shown in Fig. 2 are the experimental evidence of the long-range correlations.



(a)



(b)



(c)

FIG. 2. (a) Quasifractal network cluster of iodine deposits grown at 130 °C for 1.5 min. (b) The network cluster consisting of several distortional dendrites. (c) The closer view of the distortional dendrites.

The distortional dendrite is a composite object resulting from the regular crystal growth process and long-range correlations.

C. Amorphous fractal cluster of carbon

Fractal growth of carbon under electron irradiation is another significant example. In the present study, a piece of glass sample consisting of soda, lime, alumina, titania, and silica has been examined by using a transmission electron microscope (TEM)—Philips 300. This TEM was kept with a base pressure of 10^{-5} Torr. As in most vacuum systems, the contaminant that existed in the vacuum of the microscope column was hydrocarbon. The thickness of the glass sample is between 70 and 80 nm. Its thermal conductivity is 1

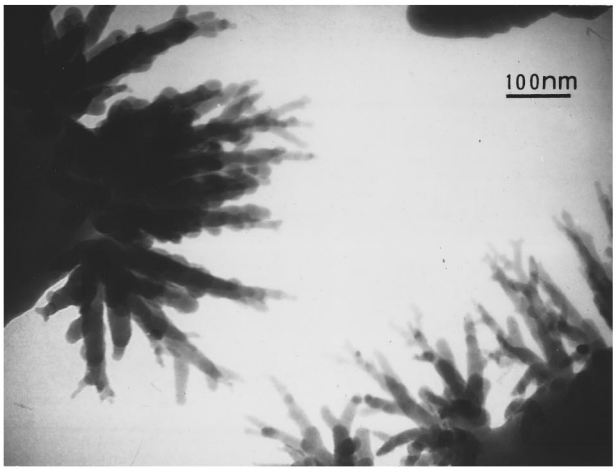


FIG. 3. TEM micrographs of the bushlike carbon clusters. (a) Morphology of the sample bombarded for 5 min. (b) Closer view of the self-similar branched structure shown in (a).

W/m kelvin approximately, and the specific conductivity is below 10^{-15} $\Omega^{-1}\mathrm{m}^{-1}$ [18]. The sample was bombarded with an electron beam of energy 100 keV. The current density was typically 10^6–10^7 $\mathrm{A/m}^2$. Several bushlike carbon clusters started to grow up at the edge of the sample when it was bombarded for 5 min with an electron beam. These clusters were of self-similar branched structure, and grew up rapidly. TEM images in Fig. 3 show the morphology of the bushlike clusters. It is seen from Fig. 3(a) that a black arch region matching the sample's edge existed at the lower left of the image. Figure 3(b) is a closer view of the bushlike cluster at a magnification of 100 000. The dimension of the bushlike cluster is between 260 and 400 nm. Each cluster consisted of a branched structure, and displayed ''dilation symmetry.''

By contrast to the glass sample, when a sample with good electrical conductivity, such as a metal sample, was tested using the same TEM equipment as well as the same experimental conditions, such a bushlike cluster was not observed except in the form of a thin layer of carbon deposited on the sample surface, especially on the edge.

The glass samples that were bombarded with an electron beam were analyzed by a scanning transmission electron mi-

roscope (STEM) equipped with an XEDS system in order to determine the composition and crystalline structure of the bushlike cluster. The results of the analysis indicated that the bushlike cluster is an amorphous substance. It is reasonable to deduce that under electron irradiation, the polymerized hydrocarbons decompose within a short time and amorphous carbon is left. These bushlike clusters were the fractal aggregates of amorphous carbon.

The growth process of amorphous carbon fractal clusters was quite different from that of molybdena and iodine, although all of them grew under nonequilibrium conditions. The glass sample is a good insulator. It emitted a lot of secondary electrons, and held a local electrical field and temperature field during an electron bombarding. It is indicated by calculation and experimental investigation that the sample temperature can reach the melting point of glass [19]. The hydrocarbon molecules remaining in the TEM column could be absorbed onto the irradiation surface from vapor phase. This local electrical field attracted the nearby hydrocarbon molecules diffusing towards the edge of the sample. Both of the long-range correlations and concentration fluctuation of hydrocarbon molecules were satisfactory for nonequilibrium growth, and fractal aggregation could occur. It is reasonable to consider the local electrical field as a nonuniform one. The distribution of the local electrical field was corresponding to the shape of the sample's edge. This could be deduced from the black arch region matching the sample's edge, as shown in Fig. 3(a). The amorphous carbon bushlike clusters began to grow up because of aggregation of the carbon atoms. The final interfacial pattern resulted from the interaction between the microscopic and macroscopic levels.

III. SUMMARY

The molybdena stacking-fractal clusters consisting of numerous whiskers or ribbonlike single crystals were observed during vapor-solid transformation. The combination of the concentration fluctuation and long-range correlations of molybdena molecules resulted in the self-similar two-dimensional fractal pattern. This is a kind of new fractal aggregation, and could be explained by the nucleation-aggregation model. The growth rate of the fractal cluster was controlled by a stacking process.

The dominance of long-range correlations is self-evident in the growth of the iodine quasifractal network cluster and its distortional dendrite during vapor-solid transformation. The distortional dendrite is a composite object resulting from the regular crystal growth process and long-range correlations.

The amorphous fractal cluster of carbon grew up due to the local electrical field, temperature field, long-range correlations, and concentration fluctuation of hydrocarbon molecules. But the oriented aggregation of carbon atoms under the local electrical field is the dominant factor in the formation of an amorphous fractal cluster. The experimental results indicate that the crystallographic structure of a fractal cluster depends on its growth condition. The fractal growth in a system sufficiently far from equilibrium can produce an amorphous fractal cluster.

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