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LETTER TO THE EDITOR

Fractal characteristics of nickel chloride deposits

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Abstract. Ramified fractal structures of nickel chloride have been observed experimentally using vapour deposition. Each fractal pattern consisted of numerous long crystals which stacked together in a regular order and formed a self-similar structure on a ceramic substrate during the phase transition. These structures were strongly dependent on the surface roughness of the deposit substrate. No fractal pattern forms on a mirror-face substrate. The experimental results show that a nucleation–aggregation (NA) model can be used to explain well the self-assembly at the vapour–solid interface.

Recently, fractal geometry has emerged as an essential concept in the understanding of the kinetic growth of disordered materials. Disordered materials often display 'dilation symmetry'; that is, they look geometrically self-similar under a transformation of scale, such as the changing of the magnification of a microscope. Some fractal structures have been obtained experimentally in real physical systems [1–3]. Several models of kinetic growth have been developed, based on experimental observation and computer simulation [4–8]. Three growth rules were usually considered: diffusion-limited aggregation (DLA), gas-phase aggregation (ballistic growth) and reaction-limited growth.

Gas-phase aggregation of disordered materials is studied in our laboratory. Different fractal patterns of molybdena crystal have been observed at vapour–solid interfaces during phase transitions [9–12]. In that experimental system, the fractal growth of molybdena crystals is basically of ballistic growth type. The monomers are more likely to penetrate into the interior of a cluster than in diffusion-limited growth, resulting in more compact structures having larger fractal dimensions. The fractal dimensions of molybdena clusters range between 1.83 and 1.96: these values are much larger than that predicted by the DLA model in two dimensions ($D = 1.67$). Stack-like formations and compact network structures were obtained on the surface of the same substrate.

On the basis of the experimental and computer simulation results, a nucleation–aggregation (NA) model was suggested in an attempt to explain the observation of molybdena fractal clusters at vapour–solid interfaces. In the NA model, some of the monomers nucleate, forming a tiny crystal or whisker, or even a cluster when a random unit lands on a site neighbouring a seed, thereby increasing the seed size.

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The NA model allows a tiny crystal (or whisker) to deposit randomly over the whole growing pattern, including in its interior. It is similar to the random rain model as regards the random deposition [8].

In this work, we report a new experimental study of nickel chloride fractal growth, and compare it with the molybdena results.

The experiment was carried out using vapour deposition equipment similar to that used in the molybdena investigation [11]. Nickel chloride powder was used as the source material, and heated at 680 °C and 750 °C for 1.1 h and 2 h respectively. The saturated vapour pressure of nickel chloride is 1 mm Hg at 680 °C.

Machinable ceramic plates with either a mirror-face surface or a smooth surface were employed as the deposit substrates in order to determine the effect of the surface roughness of the substrate. Most of the ceramic plates were set horizontally above the evaporation source, but one of them was inclined at an angle of about 60° to the horizontal plane. The system was program cooled from the selected temperature to 450 °C at a rate of 2 °C min^{-1}, and from 450 °C to room temperature at 5 °C min^{-1}.

The morphology and structural characteristics of the patterns grown were observed by scanning electron microscopy (SEM). The fractal dimensions of the fractal structures were calculated using a Model-75 computer from International Imaging Systems.

Several ramified patterns were observed on the machinable ceramic plate with a smooth surface after each experiment. However, nothing was found on a deposited substrate having a mirror-face surface after heating to 680 °C or 700 °C.

In one test, both the mirror-face substrate and the smooth-surface one were put in the same experimental system. The result found was that there were some fractal patterns on the smooth surface, but nothing on the mirror-face substrate. This shows that the fractal growth in the vapour phase depends strongly on the surface roughness of the deposit substrate. There are no nucleation sites on a mirror-face surface; therefore aggregation cannot take place on it.

The $NiCl_2$ branches grown on a smooth surface deliquesce easily in moist air, because nickel chloride is a deliquescent compound. It should be put in a drier immediately after being taken from the resistance furnace.

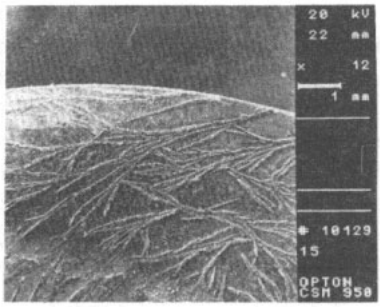

Figure 1. Self-similar structure of $NiCl_2$ grown at 680 °C for 1.1 h.

Figure 1 shows a SEM photograph of a self-similar structure of $NiCl_2$ grown at 680 °C for 1.1 h. The ceramic plate was inclined at an angle of about 60° to the horizontal plane during the vapour deposition process. Before SEM examination, the ceramic plate was coated by a conducting Au layer 10 nm thick, in order to produce a clear image. The photographs were analysed using an International Imaging System Model-75 computer in order to evaluate the fractal dimension of these fractal

structures. The fractal dimension of the pattern shown in figure 1 was $D = 1.75$. This is larger than the value predicted by the DLA model for two dimensions ($D = 1.67$). The lengths of the branches were up to several millimetres. The widths of the branches ranged between 25 and 50 μm.

The elegant spike-like pattern shown in figure 2 was observed on the same deposited substrate surface on which the branch-like structure shown in figure 1 grew simultaneously at 680 °C for 1.1 h. This spike-like pattern consisted of numerous $NiCl_2$ grains that were 35–140 μm in length and 2–40 μm in width. Also, many ballistic traces can be seen clearly on the lower left-hand side of the spike-like structure. These traces were ended by two long $NiCl_2$ clusters. The shape of the spike-like structure was affected strongly by the surrounding clusters. On the other hand, the structure could grow only in an unoccupied region.

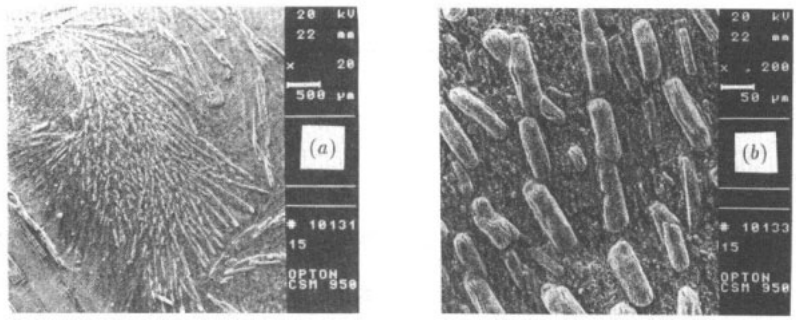

Figure 2. Spike-like patterns of $NiCl_2$ grown at 680 °C for 1.1 h: (*a*) general view; (*b*) closer view.

The fractal dimension of the spike-like structure was $D = 1.93$. From figure 2(*b*), it can be seen that most of the $NiCl_2$ grains were separated on each linear trajectory. It can be inferred that many seeds were formed at the beginning of the growth process, then grew continuously, and finally produced a spike-like pattern.

A branch-like structure grown at 700 °C for 2 h is shown in figure 3. It can be seen from figure 3 that, in general, the sizes of the branches varied widely—from 20 to 40 μm. Some of the branches were much wider than others. The whole structure is not as uniform as those shown in figures 1 and 2. The pattern for this structure is a quasi-fractal. It is reasonable to assume that a larger vapour pressure and higher deposition rate at 700 °C gave rise to the quasi-fractal pattern.

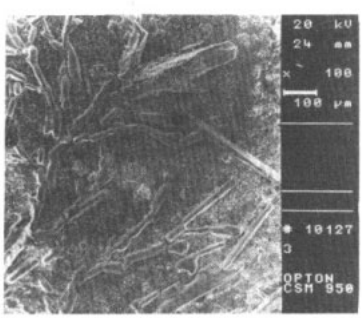

Figure 3. Ramified structure of $NiCl_2$ grown at 700 °C for 2 h.

The nucleation–aggregation (NA) model can be used to explain the growth processes of $NiCl_2$ fractal structure.

In the vapour-deposited system, numerous monomers (molecules or molecule groups) move randomly during heating of the source material. They deposit on a smooth surface of substrate, nucleate, and form seeds. The seeds grow continuously along with the deposition of the following monomers, and finally aggregate in a fractal pattern.

The formation of a fractal pattern in the vapour phase will depend only on the surface roughness of a deposited substrate. There will be no fractal pattern on a mirror-face substrate because no nucleation can take place on it. The shape of the fractal pattern will depend on temperature (or growth rate), surrounding growth, and fluidic characteristics of the vaporous monomers.

In summary, various fractal structures of $NiCl_2$ were observed on a smooth surface of the machinable ceramic plates, but there were none on a mirror-face substrate. The fractal structures could grow only in unoccupied regions, and were affected strongly by the surrounding clusters. The fractal dimensions of the self-similar structures ranged between 1.75 and 1.93.

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