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Crystal morphology of ternary compound (Cr, Fe)$_5$Si$_3$ obtained by *in situ* chemical vapour deposition

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Ternary compound crystals of (Cr, Fe)$_5$Si$_3$ were obtained on a quartz substrate by the *in situ* CVD process using *in situ* reaction of the stainless steel 410 powder, Si_2Cl_6 and hydrogen, and its crystal morphology was examined in some detail. Crystals with various interesting morphologies, such as spiral, conical, rose-like, seaweed-like, globefish-like, etc., were obtained. The most commonly observed growth habits of the crystals were spiral, conical and seaweed-like crystals.

1. Introduction

It has been found that new ternary compound crystals of (Cr, Fe)$_5$Si$_3$ can be obtained easily by the diffusion process in which the stainless steel plates (SUS 302, 304 and 310) were vapour-phase siliconized using a gas mixture of Si_2Cl_6 and hydrogen at temperatures of 1000 to 1100 °C [1, 2]. The crystals obtained were, in general, pillar-like with a hollow, and were far more stable to concentrated HCl solution than high nickel stainless steel.

It was also found that Cr–Si system compound crystals could be obtained easily by *in situ* chemical vapour deposition (CVD) in which some of the constituents of the crystals to be grown were prepared *in situ* very close to the crystal growth region [3, 4]. This crystal growth process using *in situ* CVD is considered to be very useful for obtaining new crystals which are very difficult to obtain by other growth processes.

In this work, ternary compound crystals of (Cr, Fe)$_5$Si$_3$ were obtained on a quartz substrate by *in situ* CVD using *in situ* reaction of the stainless steel 410 powder, Si_2Cl_6 and hydrogen, and its crystal morphology was examined in some detail.

2. Experimental procedure

The apparatus used and the crystal growth pattern obtained by *in situ* CVD are schematically shown in Fig. 1. Powder of the stainless steel 410 (Cr 13%, average grain size 5 μm) was dispersed in the quartz boat which was positioned in the central part of the horizontal reaction tube (quartz, 23 mm i.d.) heated from the outside by a nichrome element. The quartz boat was also used as a substrate for crystal growth. Gas flow rates of Si_2Cl_6 and hydrogen were fixed at 0.057 and 1.6 ml sec^{-1}, respectively, and the reaction time was fixed at 30 min.

3. Results and discussion

The ternary compound crystals of the Cr–Fe–Si system were *in situ* grown on the inner wall of the quartz boat (Fig. 1, region D). X-ray diffraction patterns showed that the crystals obtained were (Cr, Fe)$_5$Si$_3$ phase (hexagonal) [2]. The composition of the crystals obtained was roughly estimated to be $(Cr_{0.3}Fe_{0.7})_5Si_3$ by electron probe microanalysis. This composition is nearly the same as $(Cr_{0.23}Fe_{0.77})_5Si_3$ of the crystals obtained by vapour-phase siliconizing of the stainless steel 302 plate (Cr 18%, Ni 8%).

At temperatures of 900 to 1000 °C, polycrystals were deposited on the inner wall of the quartz boat. The well-formed crystals, with varying morphology, grew among the polycrystals at a temperature of 1100 °C. Therefore, the growth temperature of the crystals was fixed at 1100 °C.

Figs 2a and b show the side and top views, respectively, of a hexagonally formed conical crystal with a hollow. The crystal grew conically to about 20 to 30 μm in height, followed by formation of an hexagonal pillar-like form. One of the prismatic faces was frequently missing, and both rims were spiralled on the inside (Fig. 2b). A spiral growth pattern can also be seen in the bottom of the conical crystal (Fig. 2b, arrow). Fig. 3 shows the well-formed spiral crystals in which one of the prismatic faces was spiralled three times on the inside. Many downy hair-like crystals, about 1 μm long, were observed on both the outer surface of the hexagonal prismatic faces and the top face of the crystal. Spiral growth, as shown in Fig. 3, is one of the representative growth patterns frequently observed on the ternary compound crystals of (Cr, Fe)$_5$Si$_3$.

Another characteristic growth pattern of the (Cr, Fe)$_5$Si$_3$ crystal is the conical growth of a thin plate-like crystal. It was frequently observed that new thin plate-

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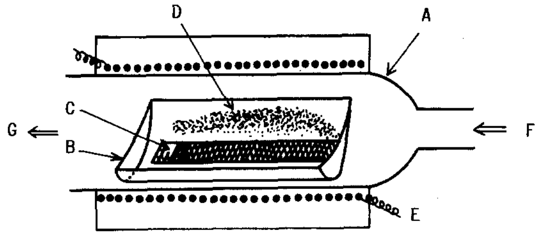


Figure 1 Schematic illustration of the apparatus used. A, Reaction tube (quartz, 23 mm i.d.); B, quartz boat; C, SUS 410 powder; D, crystal growth region; E, electric furnace.

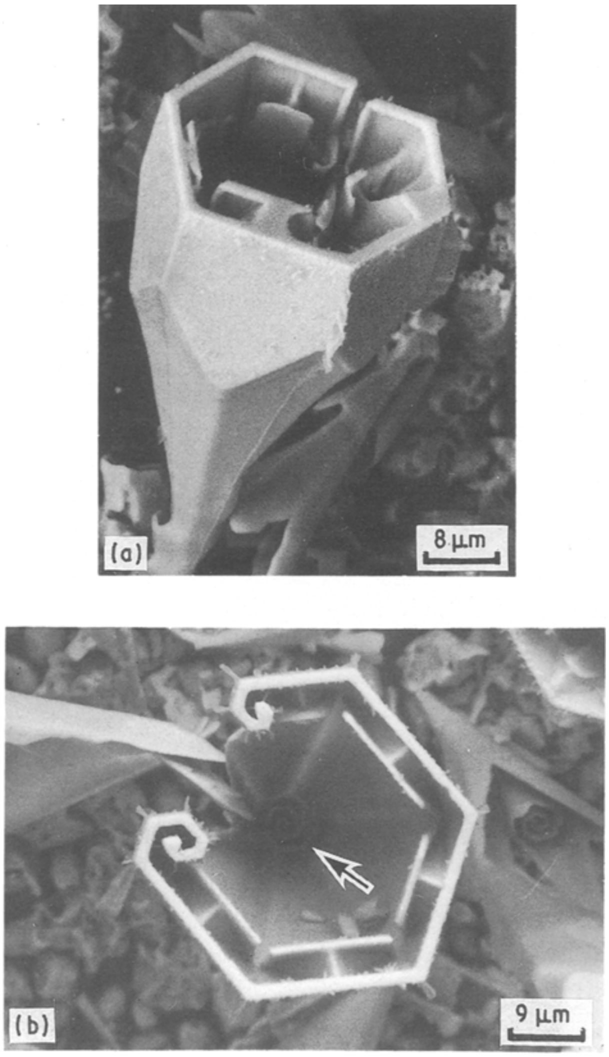


Figure 2 Hexagonal conical crystals.

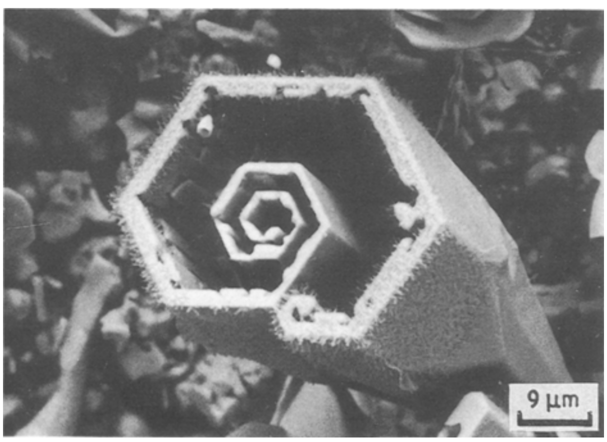


Figure 3 Hexagonal spiral crystal.

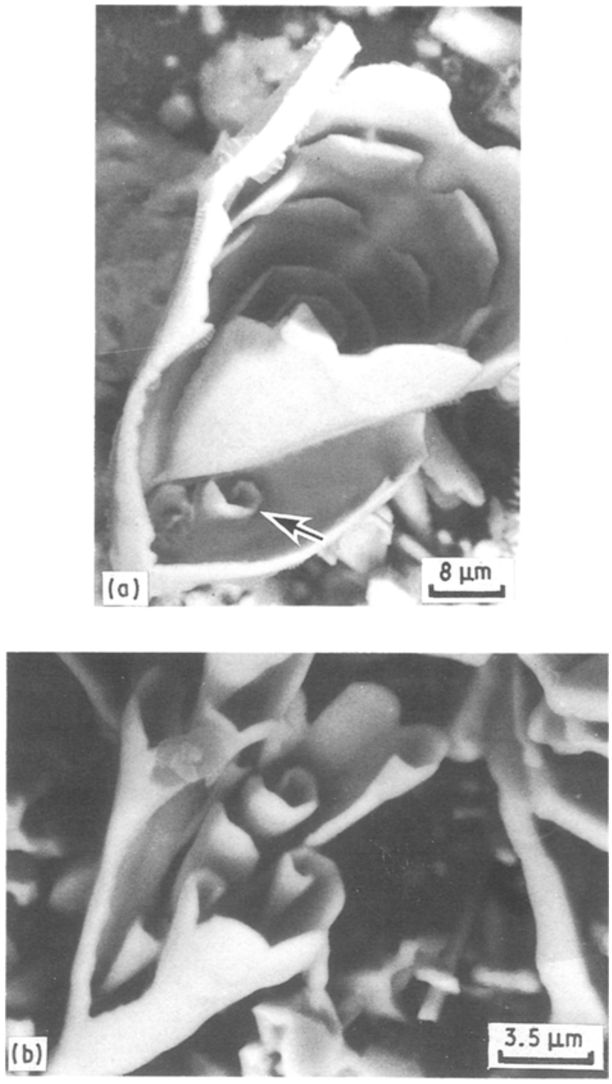


Figure 4 Conical growth of a thin plate-like crystals.

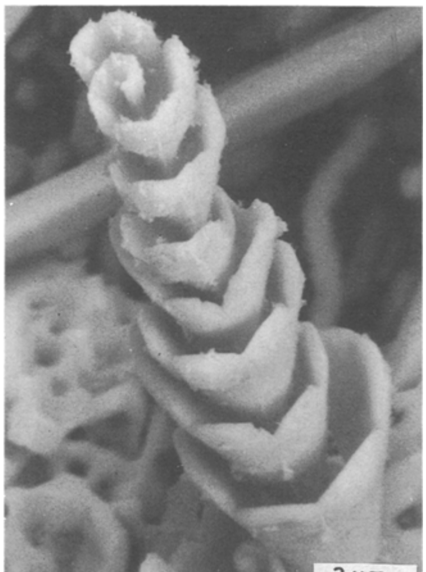


Figure 5 Stacked conical crystals.

like crystals or spirals grew from the inner wall of the original conical crystals (Fig. 4a), or thin plate-like conical crystals were divided into many new crystals curled on the inside (Fig. 4b). Such crystals are crystal-

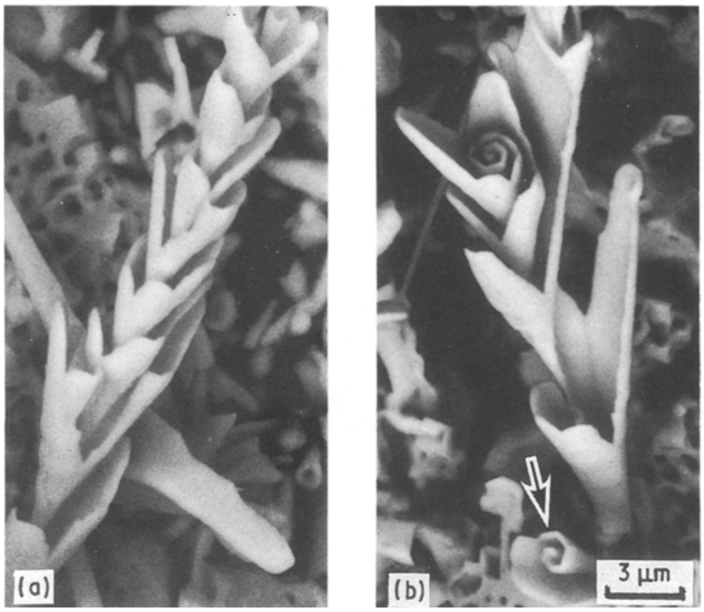


Figure 6 Successively spiralled thin plate-like crystals along the crystal axis.

lographically coherent with one another, i.e. they are a single crystal, because edges of hexagonal spirals are parallel to each other.

Fig. 5 shows a stacked conical single crystal. This crystal array is produced by successive growth of new conical crystals with constant crystallographic regularity from the inner wall, especially from the near bottom, as shown by an arrow in Fig. 4a, of the original conical crystal. The conical crystals have a nearly hexagonal form. A spiral-like growth pattern can also be seen on the top of the crystals.

Fig. 6 shows successively spiralled pillar-like crystals which were considered to have grown by the successive conical spiral growth of the thin plate-like crystals along the crystal axis. One sheet of the plate-like crystal continues from the root to the top of the pillar-like crystals. These pillar-like crystals were the most frequently observed of the many crystals present in this work. Part of the rim of the conical crystals sometimes showed outstanding growth, and spirals were found on top of the crystals, resembling a beautiful wild flower (Fig. 6b). The length (height) of these successively spiralled crystals was only about 20 to 50 μm.

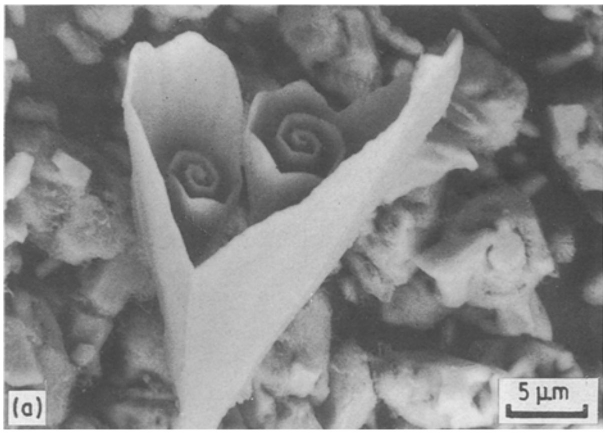
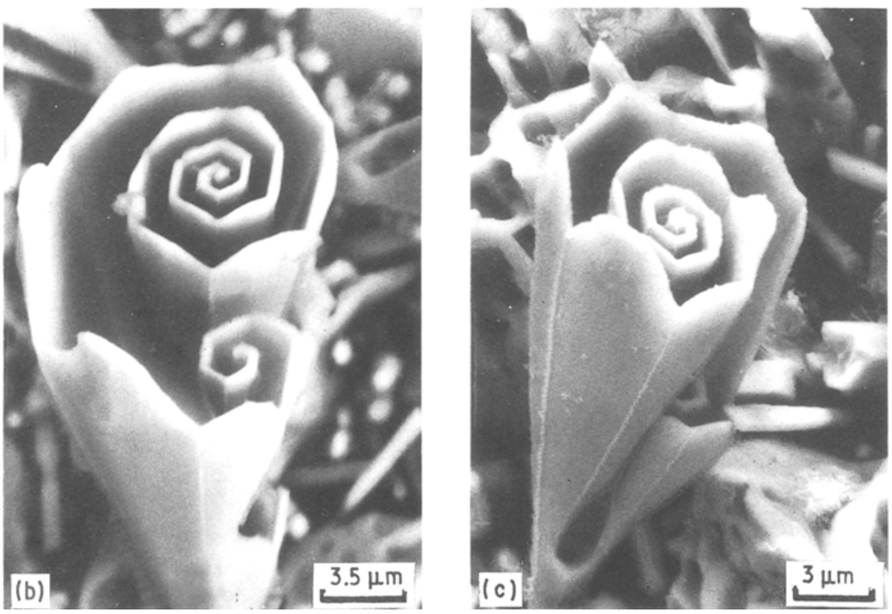
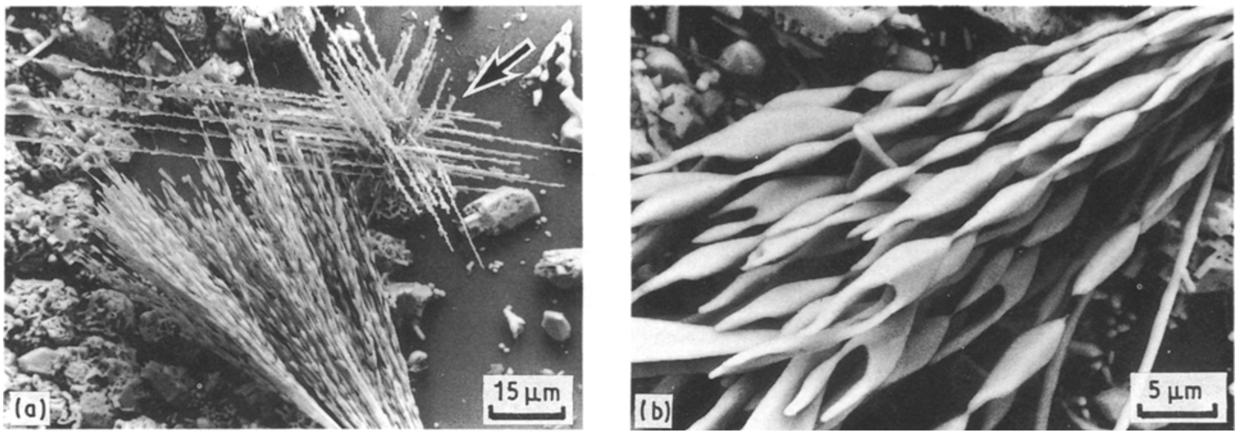


Figure 7 Double spiral "rose-like" crystals.





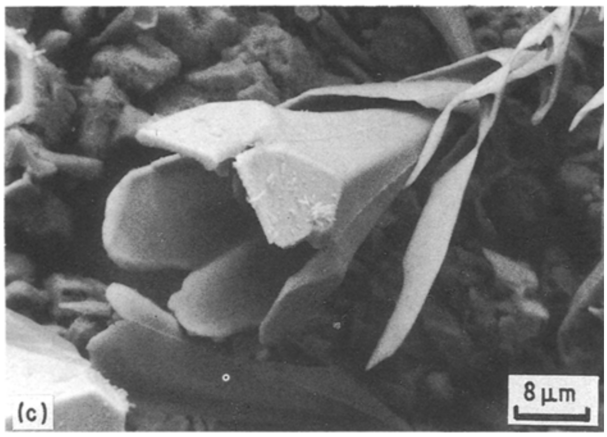


Figure 8 Fibrous or seaweed-like crystals.

Double spiral growth patterns were occasionally observed on the conically grown plate-like crystals, and representative well-formed crystals are shown in Fig. 7. Spiral patterns of a maximum of 4.5 turns were observed (Fig. 7b). These spirals usually have a regular hexagonal form. The rims of the crystals or spirals were usually not the same level but some of them jutted out, giving these double spiral crystals the look of attractive roses made of fine ceramics. These double spiral crystals were also very small being only about 20 to 50 μm high.

The third characteristic growth pattern of the (Cr, Fe)$_5$Si$_3$ crystals was fibrous or seaweed-like growth. These crystals showed a periodic thick and thin growth as shown in Figs 8a and b. The crystals always grew as bundle-like collections, some crossing each other at a constant angle (60° or 120°) (Fig. 8a, arrow). Fig. 8b shows a bundle of seaweed-like crystals. The tip of the seaweed-like crystals sometimes grew very large, forming flower-like crystals as shown in Fig. 8c. Generally seaweed-like crystals began to grow in a slanting or lateral direction against the surface from one point of the substrate surface, and branched many times during growth to form a bundle of seaweed-like crystals. Similar growth patterns shown in Fig. 9 seem to be past of this growth process. Initially, two long and slender crystals grow from the rims of a conical crystal (Fig. 9a), and then the tip of the crystals again branch (Fig. 9b). This branching is repeated many times (Fig. 9c $\rightarrow$ d) and seaweed-like crystals are formed.

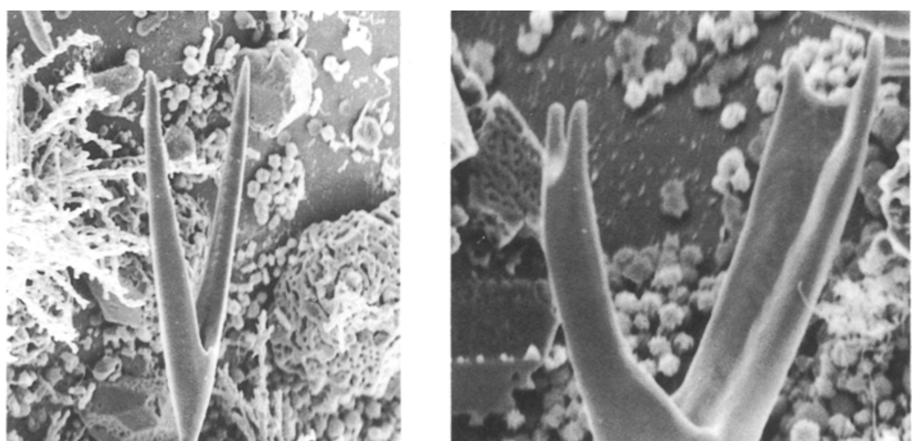


Figure 9 Growth patterns of seaweed-like crystals.

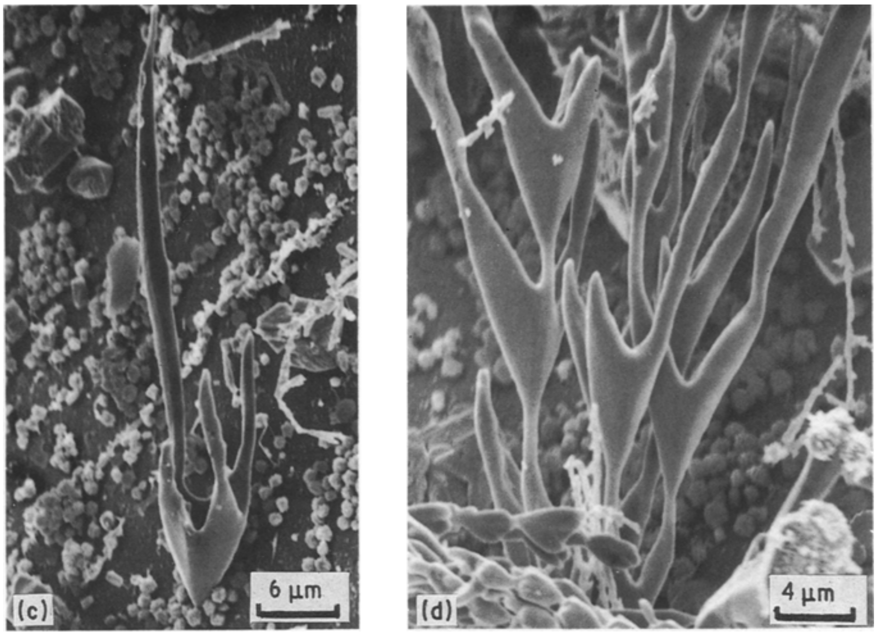


Figure 9 Continued.

Fig. 10 shows the most interesting and peculiar growth pattern of the crystals. Fin-like thin crystals about 4 to 5 µm high grew from all corners of the hexagonal hollow crystal. One of the prismatic faces spiralled hexagonally on the inside, and the thin fin-like crystals grew from the hexagonal corners. Similar crystals, resembling fish fins, were observed on Cr–Si system compound crystals obtained by *in situ* CVD, and were considered to be amorphous silicon from the results of a selected-area electron diffraction pattern and electron probe microanalysis [5]. It may be reasonably considered that the fin-like crystals shown in Fig. 10 are also amorphous silicon, and that they grew rapidly at relatively low temperatures as stopping the reaction. This crystal has the look of a globefish or an angler fish with a fully open mouth. Other crystals with very interesting morphology, such as tulip or onion-like (Fig. 11a), starfish-like (Fig. 11b), catfish-like, tadpole-like, octopus-like, etc., were also observed.

Many crystals were obtained with various kinds morphology under the same growth conditions. That is, many crystals presented in this work were obtained during the same experimental run and at the same time, on the small growth region (about 5×5 mm^2). These results indicate that crystal growth and morphology using *in situ* CVD are very sensitive to some microscopic conditions of the growth atmosphere,

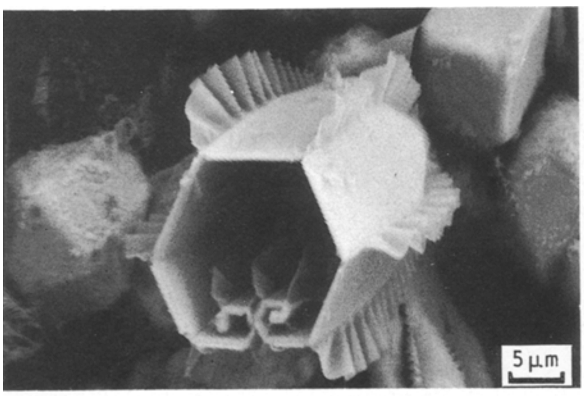


Figure 10 An interesting hexagonal hollow crystal with fin-like crystals on the corners.

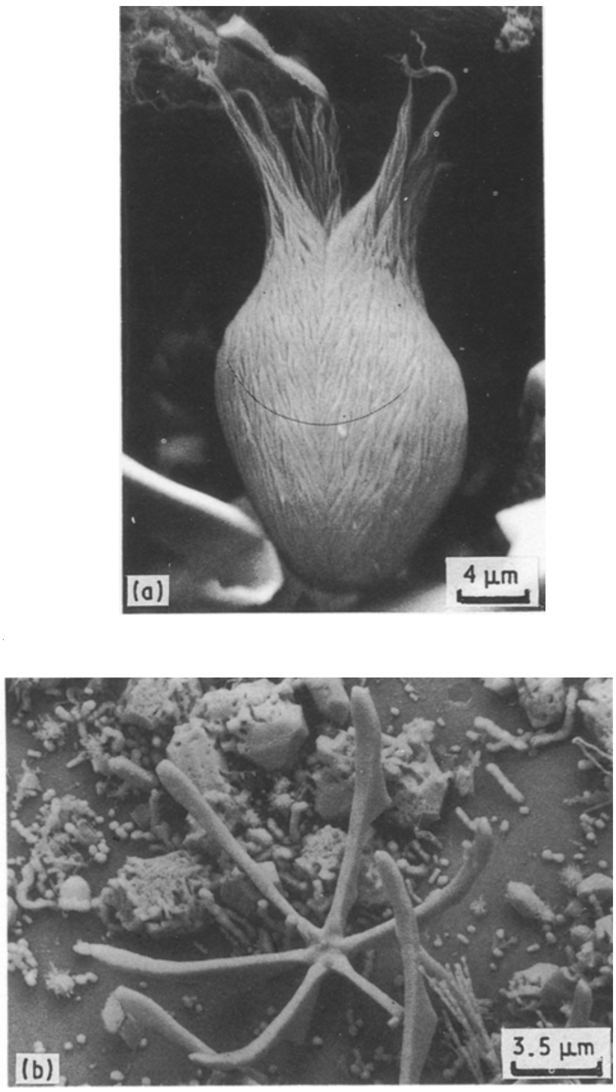


Figure 11. Some interesting crystal morphologies.

substrate surface, etc. The crystals obtained in this work were generally very small, about 20 to 50 μm high. However, the microscopic morphology of the crystals was both very beautiful and attractive.

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