Electron Microscopic Studies of Growth Structures in Hexagonal Ferrites

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Electron microscopic studies of sintered hexagonal ferrites have revealed growth structures which indicate that crystal growth from a relatively highly saturated vapor phase occurs above certain temperatures during the sintering process. Illustrations of variations in the growth structures at various locations in the ferrite are given, and the probable importance of the vapor-phase growth mechanism in the over-all sintering process is discussed.

I. Introduction

DURING an investigation of the sintering of hexagonal ferrites (barium ferrite and ferroxplana)[1] it was observed that above certain temperatures the rate of growth of individual grains was too great to be explained by diffusion in the solid state alone. A decrease in bulk density which accompanied the increase in grain size could be explained by a surface-diffusion mechanism. However, further examination by light and electron microscopy has revealed the presence of a type of structure typical of a vaporization and condensation mechanism rather than one of volume or surface diffusion.

II. Microscopic Examination

Figure 1 shows photomicrographs of grains on the surfaces of two different hexagonal ferrites, CoZ ($3BaO \cdot 2CoO \cdot 12Fe_2O_3$) and CoY ($2BaO \cdot 2CoO \cdot 6Fe_2O_3$), which had been sintered at 1250°C. The elevations and depressions typical of growth from vapor, solution, or melt were observed under the microscope. No evidence of melting was found and the grains did not grow from a solution. It therefore seemed likely that vaporization and condensation had occurred. Further examination by electron microscopy seemed to be warranted.

III. Electron Microscope Examination

The study of individual grains of different hexagonal ferrite compositions by electron microscopy revealed evidence of two different mechanisms of crystal growth: (1) growth from a vapor with a relatively high degree of supersaturation, as mentioned above, and (2) solid-state diffusion. The writers are concerned with the first type of growth.

(1) Suggested Mechanism

The presence of negative crystals on the surface of the crystals as described in the foregoing suggests regions of energy higher than the average energy of the crystal. Such regions of higher energy may be the result of dislocations,

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[1] G. H. Jonker, H. P. J. Wijn, and P. B. Braun, "Ferroxplana, Hexagonal Ferromagnetic Iron-Oxide Compounds for Very High Frequencies," *Philips Tech. Rev.*, **18** [6] 145-54 (1956-57); *Ceram. Abstr.*, **1958**, August, p. 207*c*.

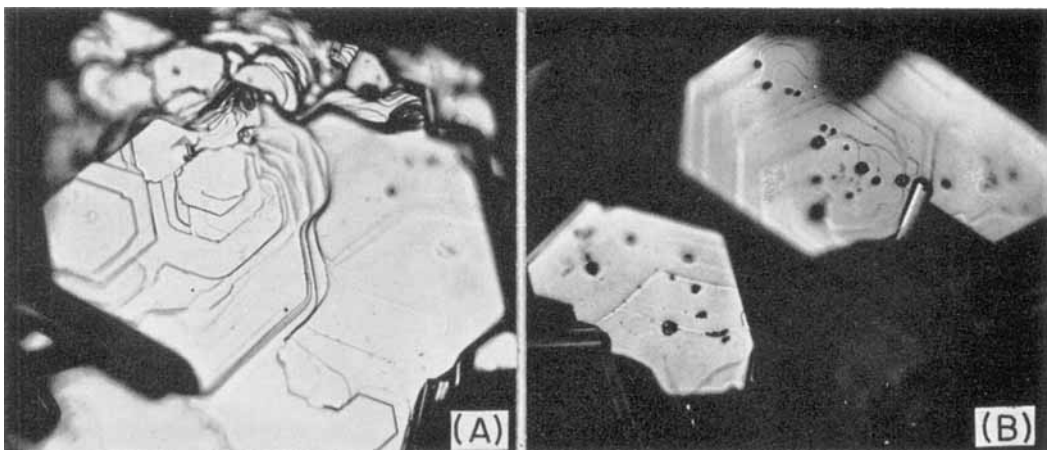

Fig. 1. Photomicrographs with light microscope of hexagonal ferrites. (A) CoZ ($3BaO \cdot 2CoO \cdot 12Fe_2O_3$) and (B) CoY ($2BaO \cdot 2CoO \cdot 6Fe_2O_3$). (×500.)

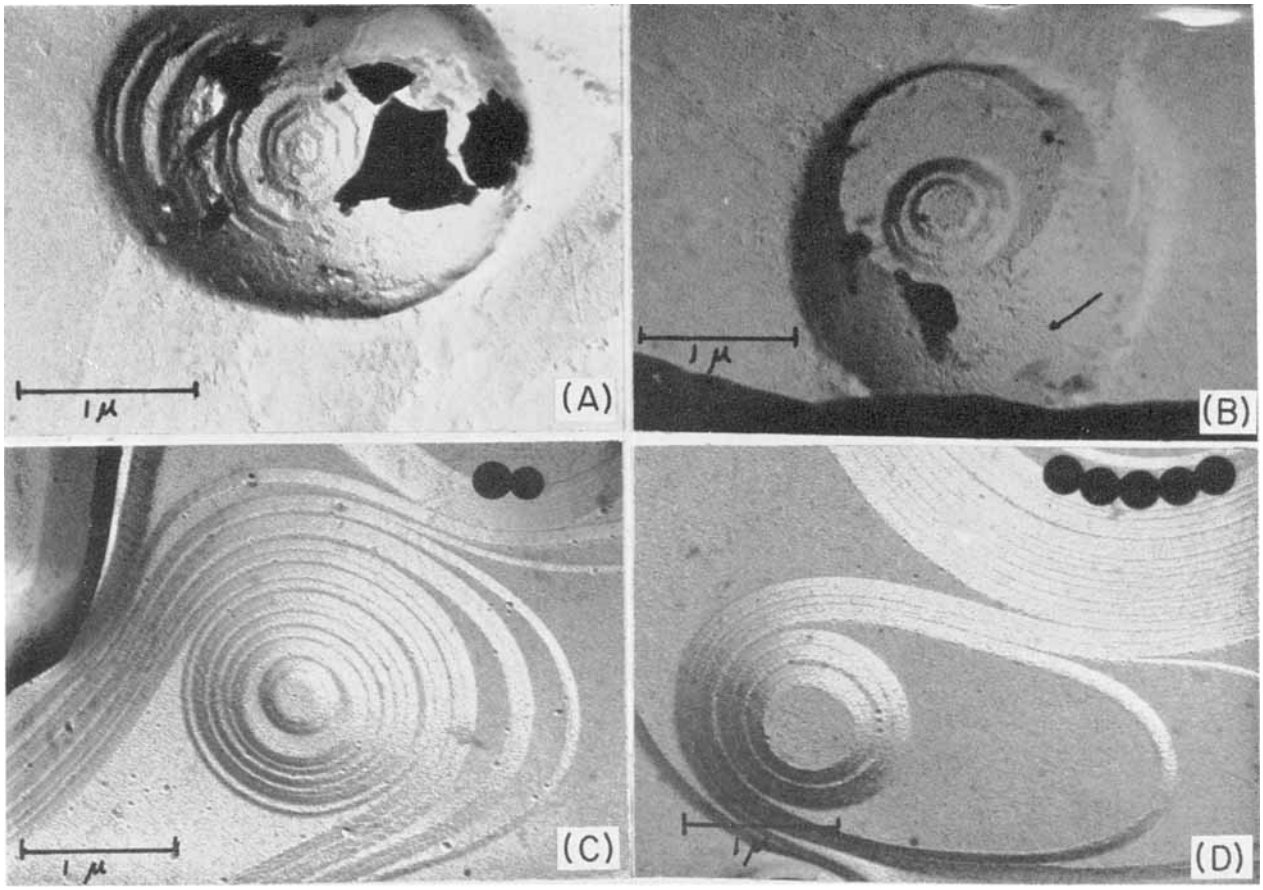

Fig. 2. Electron micrographs from interior of hexagonal ferrite specimens. (A) and (B), ZnY ($2BaO \cdot 2ZnO \cdot 6Fe_2O_3$); (C) and (D), CoY ($2BaO \cdot 2CoO \cdot 6Fe_2O_3$). (×20,000.)

chemical inhomogeneity, or other structural defects. These are regions from which material might be expected to escape to form the vapor phase. The positive stacks of plates also observed may then be formed by condensation of the vapor on regions of lower energy.

(2) Interior Grains

Grains inside the specimen showed a positive or negative cyclic stacking of plates or occasionally a spiral-like growth probably similar to that described by Lang.[2] The hexagonal shape was found only very near to the termination of the stack. This type of cyclic growth might be expected in the interior of the specimen where a relatively high degree of supersaturation of the vapor could be maintained. Figure 2 shows electron micrographs of these structures found in the interior of the specimen.

(3) Exterior Grains

Grains on the outside surfaces (Fig. 3) showed a structure more in accord with stacks of hexagonal basal plates. This indicates a much slower growth as would be expected from a lesser degree of vapor supersaturation.

(4) Thickness of Lamellas

In general, the well-developed lamellas were of uniform thickness. Although accurate measurements have not been made for individual plates, the thickness appeared to be between 0.5 and 0.1 μ. No great difference in thickness was noted between the lamellas from the surface and those from the interior of the specimens. Occasionally, incipient lamellas were observed whose thickness was much less than that of the well-developed variety. The arrow in Fig. 2(*B*) points out one of these regions.

Appendix

Replication Technique

Replication of the ferroxplana for electron microscopy presented a number of difficulties because of its porosity and the roughness of its surfaces. Several different replicating techniques were tried, but satisfactory results were obtained most conveniently and consistently by a two-stage process using cellulose acetate primary replicas and carbon secondary replicas. The cellulose acetate primary replicas were prepared by moistening cellulose acetate tape* 0.005 in. thick with acetone and press-

[2] A. R. Lang, "On the Origin of Certain Spirals of Large Step-Height Observed on Crystal Surfaces," *J. Appl. Phys.*, **28** [4] 497–98 (1957).

* The cellulose acetate tape used in this work is manufactured by the Monsanto Chemical Company under the trade name VuePak.

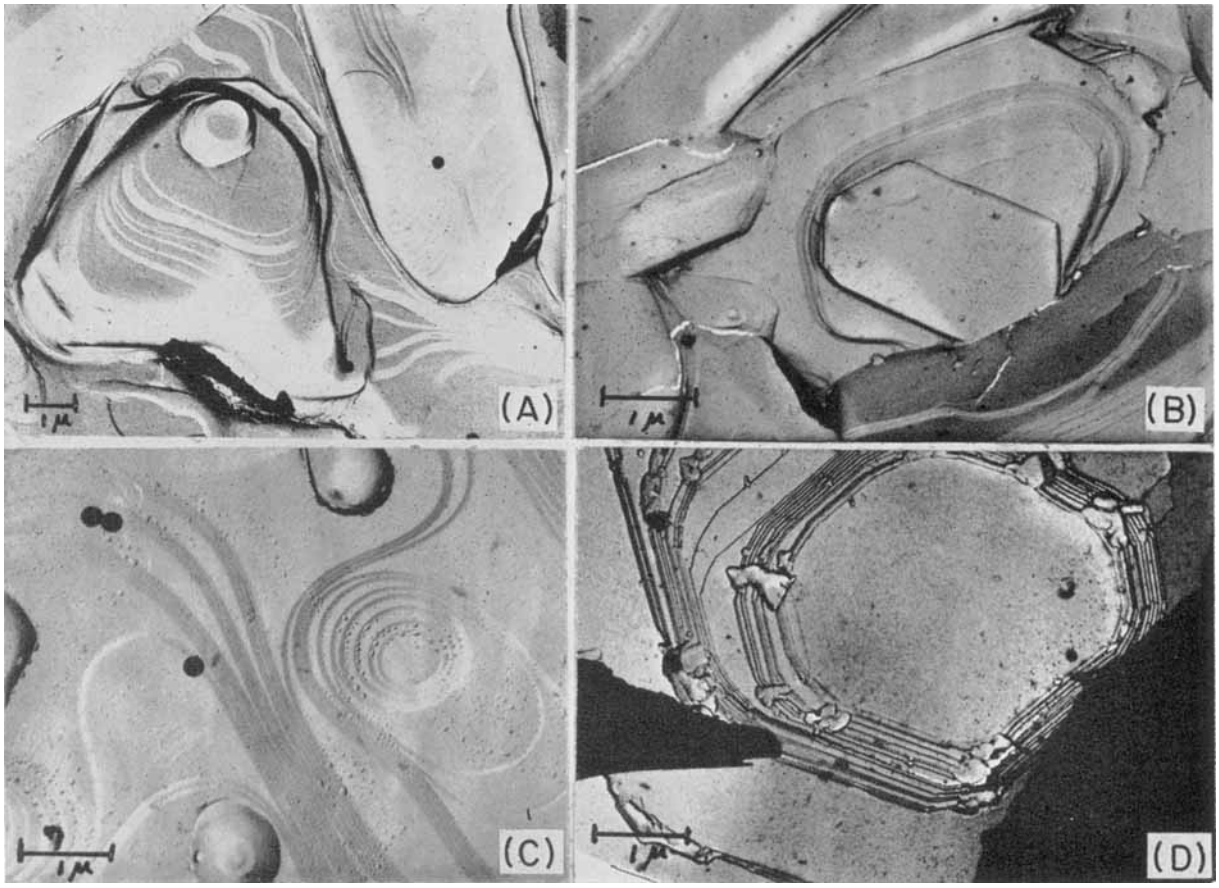

Fig. 3. Electron micrographs from surfaces of hexagonal ferrite specimens. (A) and (B), CoZ ($3BaO \cdot 2CoO \cdot 12Fe_2O_3$); (C) and (D), CoY ($2BaO \cdot 2CoO \cdot 6Fe_2O_3$). ((A) ×7000; (B), (C), and (D) ×12,000.)

ing it evenly against the surfaces of the ferrite. When dry, the tape was stripped from the surfaces and shadowed with palladium. Carbon films 600 to 800 a.u. thick were then deposited over the palladium by the method of Bradley.[3] The coated cellulose acetate tape was then cut into small squares which were placed over electron microscope specimen grids on a piece of fine-mesh screen which was inclined beneath the condenser of a Soxhlet extractor. Acetone was placed in the flask of the extractor and was heated gently so that it dripped slowly from the condenser onto the screen, dissolving the cellulose acetate and leaving the carbon replica with the shadowing metal mounted on the specimen grid ready for observation in the electron microscope. This procedure for dissolving primary replicas in a two-state replica process offers several advantages over other methods in current use.

Acknowledgment

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[3] D. E. Bradley, "High-Resolution Evaporated-Carbon Replica Technique for the Electron Microscope," *J. Inst. Metals*, **83** (Pt. 1) 35–38 (September 1954).