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THE CRYSTALLOGRAPHIC ORIENTATION OF SEVERAL MORPHOLOGIES IN THE ZINC-Mg_2Zn_{11} EUTECTIC.

(9) Technical rept.,

By

Robert

(10) R. R. Jones .

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Lafayette College
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THE CRYSTALLOGRAPHIC ORIENTATION OF SEVERAL MORPHOLOGIES IN THE ZINC-Mg_2Zn_{11} EUTECTIC

INTRODUCTION

The study of eutectic microstructures has been pursued for many years; attempts to understand the mechanism of solidification and the reasons for these structures have only recently begun to be successful. One difficulty has been the existence of several different morphologies, such as lamellar, rod-like, and chinese script. Although some investigators have postulated that the lamellar form is the equilibrium one for all pure metallic eutectics, many systems solidify in other forms; sometimes more than one is observed in the same alloy frozen under different conditions.

This investigation was undertaken in order to discover the reasons for the existence of various morphologies in the same eutectic alloy. The zinc-magnesium eutectic at three percent magnesium (by weight) and 367°C was selected for this purpose since it was known to show several different morphologies.

THEORY

Hunt and Jackson [1] have recently classified eutectics according to the mode of solidification of the pure component phases. Solids with low entropies of fusion freeze in a dendritic manner and exhibit a plane, non-crystallographic solid-liquid interface during unidirectional solidification. Solids with complex crystal structure and high entropy of fusion yield faceted or idiomorphic crystals and cannot form a non-crystallographic solid-liquid interface. Eutectics are divided into three classes with different combinations of "smooth" and "faceted" phases. The first class; both phases smooth, includes all metallic eutectics with regular morphologies. These morphologies, notably the lamellar, are produced by simultaneous solidification of both phases resulting in a structure described by Kraft[2] as "two interpenetrating single crystals."

The solidification of a eutectic alloy is controlled by the extraction of heat from the system, both the rate and direction of heat flow being important. The "driving force" for solidification is an undercooling of the solid-liquid interface below the equilibrium eutectic temperature. According to Chadwick[3], this undercooling consists of three parts: a constitutional undercooling due to rejection of solute from the growing solids; an undercooling due to the curvature of the individual phase surfaces in contact with the liquid; and an undercooling, usually neglected, due to the kinetic process of solidification. The total undercooling is characteristic of the particular system at the imposed growth rate, and is not subject to external control. When steady-state growth has been achieved, each phase will reject excess solute atoms into the liquid; in order to maintain the steady-state, these atoms must diffuse in the liquid parallel to the advancing solid-liquid interface. This process is controlled by the constitutional undercooling. Since two solid phases are growing cooperatively into the liquid, there must be a boundary between them. The surface energy of this boundary interacting with the solid-liquid surface energies, produces a groove in the solid-liquid interface and curvature in the surface of each solid. This interphase boundary energy can be minimized if the interface consists of crystallographic planes of suitable atomic population to allow "atom site matching" across it. The nature of this surface can be studied by determining the relative crystallographic orientation of the phases in unidirectionally solidified eutectics. Kraft[4, 5] has shown for two lamellar eutectics that a unique orientation relationship exists, which describes a stable, low energy interphase boundary.

In the early stages of freezing, before a steady state is reached, nuclei must form and grow in the undercooled liquid. As a nucleus of one phase grows in breadth and thickness, a zone of constitutionally undercooled liquid suitable for nucleation of the other phase is produced around it. If the existing solid can act as a nucleating agent for the other solid phase, the two will form and grow cooperatively. Mondolfo[6, 7, 8,] has shown that the solid phase with higher entropy of fusion will usually nucleate the other phase, but that the reverse is not true. Once crystals have begun to grow, further nucleation is not necessary. Branching or lateral growth of one phase across the other will take place, since growth of existing crystals requires less energy than fresh nucleation. Kraft[4] has shown that the orientation relationship between the phases changes as freezing progresses until the low energy relationship is established in the latter half of unidirectionally solidified ingots.

Several metallic eutectics solidify in either the lamellar or the rod morphology depending on the growth rate. Tiller[9] has analyzed this transition in terms of the undercoolings mentioned earlier. He concludes that the rod form allows easier diffusion than the lamellar and may be stable at high growth rates if the solid-solid interphase boundary energy is not high. Obviously a smooth cylinder cannot form a coherent crystallographic boundary with the matrix in which it grows. The resultant increase in surface energy must be balanced by a decrease in the diffusion energy for this shape to be stable. Hunt and Chilton[10] have demonstrated that any growth condition which disturbs the planar solid-liquid interface may promote rod formation in eutectics where one phase is one-third or less of the alloy by volume.

EXPERIMENTAL

Zinc (99.999% pure) and magnesium (99.97% pure) were carefully weighed out, melted together in pyrex tubes under argon, and cast into graphite boats twenty centimeters long by either nine or thirteen millimeters square. The boat and ingot were inserted into a zone leveller, remelted under an argon atmosphere, and solidified unidirectionally at predetermined rates from two to fifty centimeters per hour. The ingots were sectioned normal to the growth axis at a point from one-half to three-quarters of their length back from the first end to freeze, and these sections were prepared for metallographic examination. Most ingots had the nominal eutectic composition (checked metallographically), but some were prepared with either an excess or a deficiency of magnesium. In an attempt to produce the spiral morphology described by Fullman and Wood[11], ingots of forty to fifty grams weight were allowed to cool in the melting furnace without controlled heat flow. These were usually sectioned vertically to allow study of any segregation from top to bottom.

Crystallographic orientation relationships were determined on carefully polished, but unetched sections by the Kraft technique.[12] Suitable areas were selected on etched specimens, outlined with a stylus, and then repolished to give the best possible balance between the strong diffraction maxima from the zinc phase and the weaker ones from Mg_2Zn_{11}. Several specimens of each morphology were studied, and the results plotted on stereographic projections.

Two distinctly different types of alloy were studied; those with excess magnesium in the form of cellular or "three-vaned" dendrites of

Mg_2Zn_{11}, and those without these dendrites. In the latter case, the morphology was either lamellar or rod-like depending on the growth rate. At rates below ten centimeters per hour, only lamellae were formed in unidirectionally solidified ingots. At rates faster than fourteen centimeters per hour, only rods of zinc in a matrix of Mg_2Zn_{11} were found; at intermediate growth rates, mixtures of rods and lamellae were formed. The lamellar morphology consisted of two sets of parallel plates making an angle of about 55 degrees to each other similar to the microstructure of the Mg-Mg_2Sn eutectic described by Kraft[5]. The lamellar microstructure consisted of a few large "grains" several millimeters in cross section and a few centimeters long, each of which contained several small perfect areas separated by narrow bands of less perfect material. Both sets of lamellae within a "grain" seemed to be parallel to each other in spite of the imperfections. The rod morphology, found in this eutectic with nearly equal volume fractions of the two phases, consisted of many small, scale-shaped groups again separated by irregular or degenerate material. Under no conditions was it possible to produce large areas of either rods or lamellae without imperfections.

Alloys with three-vaned dendrites of Mg_2Zn_{11} showed areas of rods bounded by narrow bands of dendrites at high growth rates, while at lower rates the dendrites were separate rather than joined in a band, and were surrounded by both lamellar and rod areas even at growth rates where only lamellae formed in the absence of these dendrites. (Fig. 4)

In some ingots not unidirectionally solidified, spirals were formed associated with magnesium-rich primary crystals. Alloys on both sides of the eutectic composition exhibited this morphology which is reported by Hunt[13] to be caused by metastable $MgZn_2$. X-ray diffraction and metallographic studies confirmed the presence of this phase. Spirals could not be produced in unidirectionally solidified alloys, nor were they formed in alloys with the eutectic composition.

The crystallographic orientation relationships for lamellae, rods and three-vaned dendrites were found to be the same:

$$(0001)\ \mathrm{Zn} \sim\parallel (1\bar{1}\bar{1})\ \mathrm{Mg_2Zn_{11}}$$

$$(2\bar{3}10)\ \mathrm{Zn} \sim\parallel (101)\ \mathrm{Mg_2Zn_{11}}$$

Since there was within any specimen real departure from the ideal microstructure in which each particle is perfectly parallel to each other and at exactly the proper spacing, it is not proper to state that:

$$(0001)\ \mathrm{Zn} \parallel (1\bar{1}\bar{1})\ \mathrm{Mg_2Zn_{11}}$$

The variation from specimen to specimen was small however, often less than five degrees, including experimental scatter.

The lamellar specimens were found to have a growth axis $\sim\perp$ $(2\bar{3}10)$ Zn and (101) Mg_2Zn_{11} (the two planes being nearly parallel to each other as above.) (Fig. 1) It was not possible to assign a consistent set of low-indexed planes as the lamellar interfaces, of which there are two in each specimen. This lack of a "habit plane" can be explained by reference to the crystal structures. While zinc is simple in structure (close-packed hexagonal), Mg_2Zn_{11} is complex having a cubic unit cell with thirty-nine atoms. In such a crystal, many planes may be almost equally close packed and thus possess almost equally low energy. According to Mondolfo[6, 7, 8,] the phase with complex crystal structure always nucleates the simpler phase, so that the eutectic must grow from an existing Mg_2Zn_{11} crystal. Since this crystal may have any of several equally low energy planes exposed to the liquid, it is not surprising that no consistent set of interface planes was found.

The rod morphology was found to grow $\sim\perp(1\bar{1}01)$ Zn and (401) Mg_2Zn_{11} with rather more scatter than the lamellar specimens. (Fig. 2). This seems to be a less stable structure as is shown by annealing near the eutectic temperature for several days. Lamellar specimens subjected to this treatment were almost unchanged, while most of the rods coalesced into larger globular particles. In spite of experimental scatter, the growth axis of the rod morphology is significantly different from that determined for the lamellae.

The three-vaned dendrites of Mg_2Zn_{11} were found to have an axis near to a $\langle 111\rangle$ direction, the vanes being approximately parallel to $\{110\}$ planes. Since some of these specimens were frozen without control of the heat flow rate or direction, it is difficult to assign a growth direction. However, since the vanes seemed symetrical about their central axis, this was assumed to be the growth direction. Hunt [13] has compared this microstructure to a set of cubes growing with their corners foremost, which agrees well with the statement above.

No crystallographic orientation relationship could be found to fit the spiral morphology. The specimens available had only rather small "grains" little more than a millimeter in diameter, and even these showed appreciable lack of parallelism between the sides of neighboring individual spirals.

DISCUSSION

The lamellae-to-rods transition in unidirectionally frozen ingots without three-vaned dendrites of Mg_2Zn_{11} seems to be diffusion controlled. As mentioned earlier, diffusion is easier (having shorter paths in most directions) for the rod than for the lamellar morphology. Since the crystal structure of Mg_2Zn_{11} is so complex, it seems that many crystallographic planes can have nearly equally low surface energy. Thus the interface energy portion of the undercooling is not likely to be greatly increased by the lack of a plane surface between the two phases, and the easier diffusion will stabilize the rod form at faster growth rates, in spite of the almost equal volume fraction of the two phases.

In the presence of three-vaned dendrites of Mg_2Zn_{11}, the eutectic morphology is controlled by the crystallographic orientation relationships between these primary crystals and the eutectic nucleated on their surfaces as well as by the relation of the preferred growth direction to the thermal axis of the solidifying ingot. (Fig 3 & 4).

Since these dendrites extend into the undercooled liquid, there are two solid-liquid interfaces associated with each dendrite: the general interface normal to the direction of heat extraction, and a local interface between the dendrite vane and the undercooled eutectic liquid into which it is growing. This liquid is metastable and will freeze by the eutectic reaction. Zinc crystals will be nucleated on the vane surface according to the relationship: $(0001)\ Zn \parallel (1\bar{1}\bar{1})\ Mg_2Zn_{11}$, $(23\bar{1}0)\ Zn \parallel (101)\ Mg_2Zn_{11}$, and will grow in that morphology which is most favored by the thermal gradient. If these zinc nuclei have such orientation that the preferred rod growth direction, $\perp$ $(1\bar{1}01)$ Zn and $(401)\ Mg_2Zn_{11}$, is nearly parallel to the thermal axis of the ingot, the rod morphology will result, with rods growing nearly parallel to both the thermal axis and the dendrite axis. Since the rods do not grow parallel to the dendrite axis, their growth, with fresh nucleation following the general solid-liquid interface, will consume all of the liquid contained between dendrite vanes, as shown in the model, Fig. 6. If this is not the case, lamellae will grow normal to the vane surface and the local interface. This is shown in Fig. 5, a stereogram of the structure shown in figure 2. Since the lamellar growth axis is normal to $(2\bar{3}10)$ Zn and (101) Mg_2Zn_{11}, this morphology is to be expected, even though its growth is parallel to the general solid-liquid interface and does not consume the undercooled liquid as rapidly as would growth normal to this plane.

CONCLUSIONS

The zinc-Mg_2Zn_{11} eutectic posesses a unique crystallographic orientation relationship in three different morphologies: lamellar, rod, and three-vaned dendritic. This is:

$$(0001)\ \mathrm{Zn} \sim\parallel (1\bar{1}\bar{1})\ \mathrm{Mg_2Zn_{11}}$$

$$(2\bar{3}10)\ \mathrm{Zn} \sim\parallel (101)\ \mathrm{Mg_2Zn_{11}}$$

The lamellar morphology has a growth axis nearly normal to $(2\bar{3}10)$ Zn and (101) Mg_2Zn_{11} and the rod growth axis is nearly normal to $(1\bar{1}\bar{0}1)$ Zn and (401) Mg_2Zn_{11}. The three-vaned dendrites grow nearly parallel to a $\langle 111 \rangle$ direction of Mg_2Zn_{11} with the vanes nearly parallel to $\{110\}$ planes.

In the absence of three-vaned dendrites, the eutectic morphology changes from lamellar to rod-like at growth rates between ten and fourteen centimeters per hour because the shorter diffusion paths in the liquid in front of the growing rods reduce the necessary undercooling. The increase in solid interface energy seems to be small due to the complex crystal structure of Mg_2Zn_{11}.

The presence of three-vaned dendrites of Mg_2Zn_{11} which can act as nucleation sites for zinc, combines with the thermal axis and the general crystallographic orientation relationship, to determine which eutectic morphology will be formed. If the crystallographic orientation of the freshly nucleated eutectic is such that a preferred rod growth direction is nearly parallel to the thermal axis, the rod morphology will result even at growth rates which would normally favor the growth of lamellae. When the rod growth axis is not near the thermal axis, lamellae will grow normal to the dendrite vane if the growth rate is favorable. At high growth rates, alternate bands of rods and dendrites are formed.

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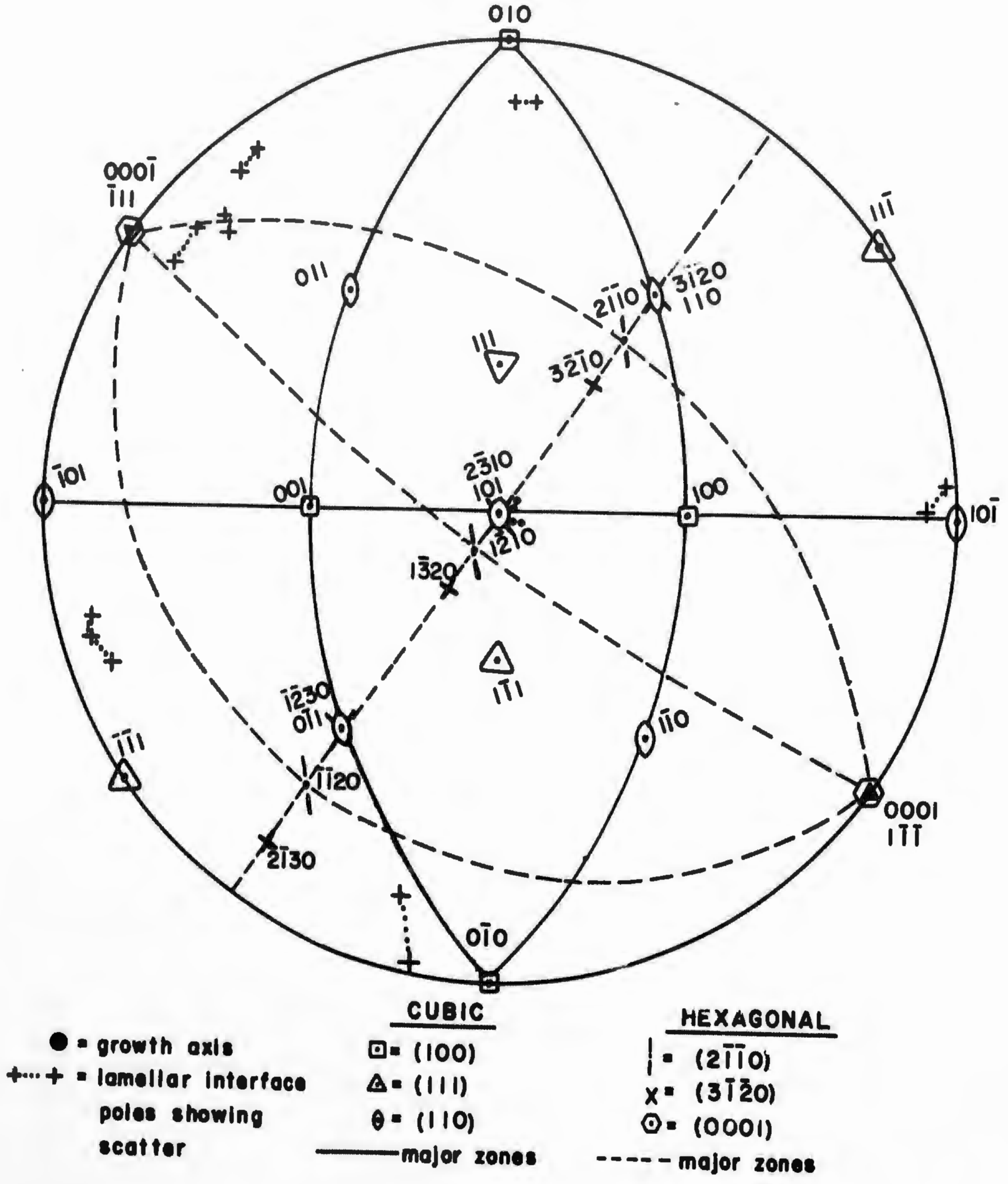

Figure 1. Combined data for four lamellar specimens showing relative orientation, growth direction, and lamellar interface poles.

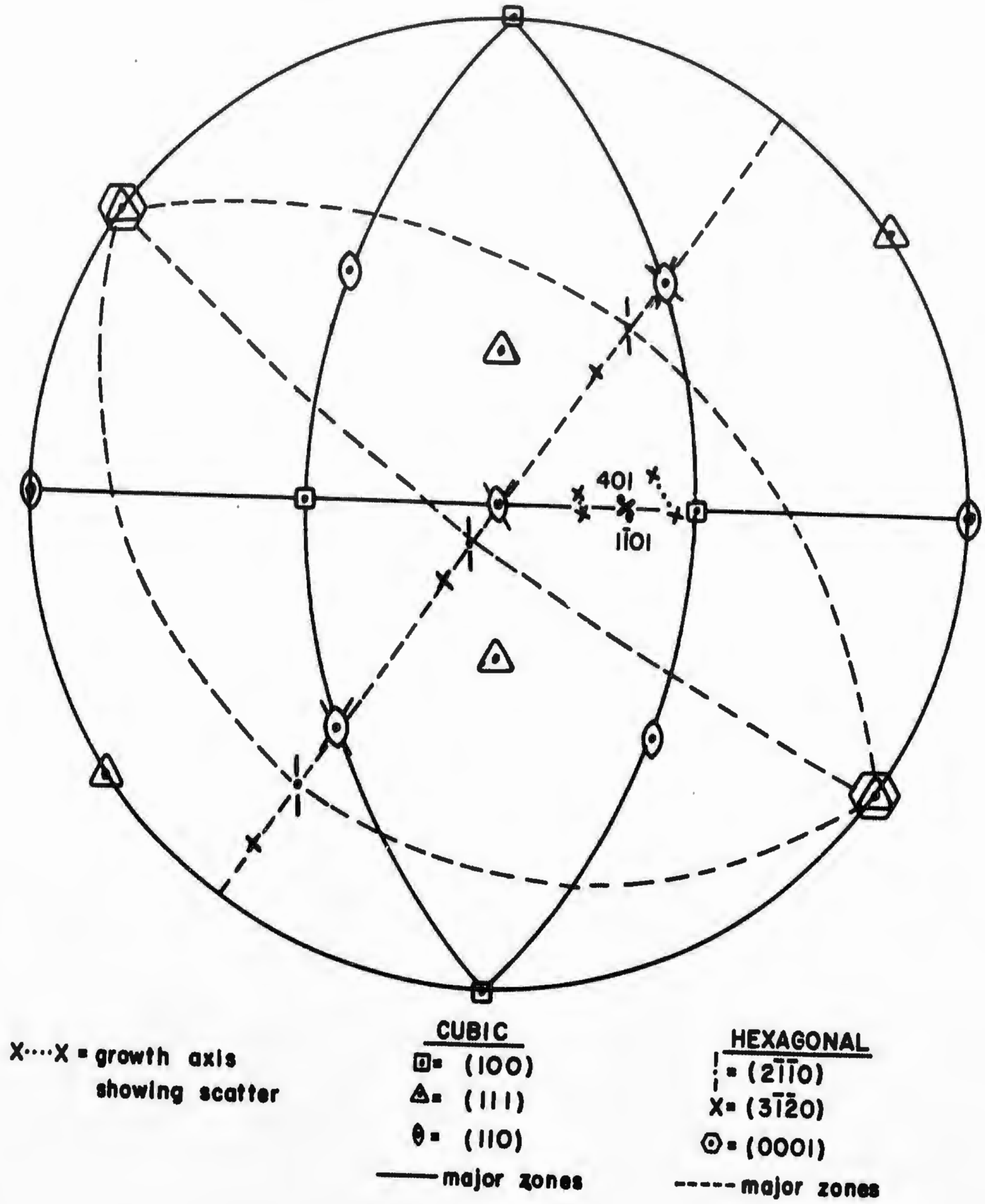

Figure 2. Combined data from three rod specimens showing relative orientation and growth direction.

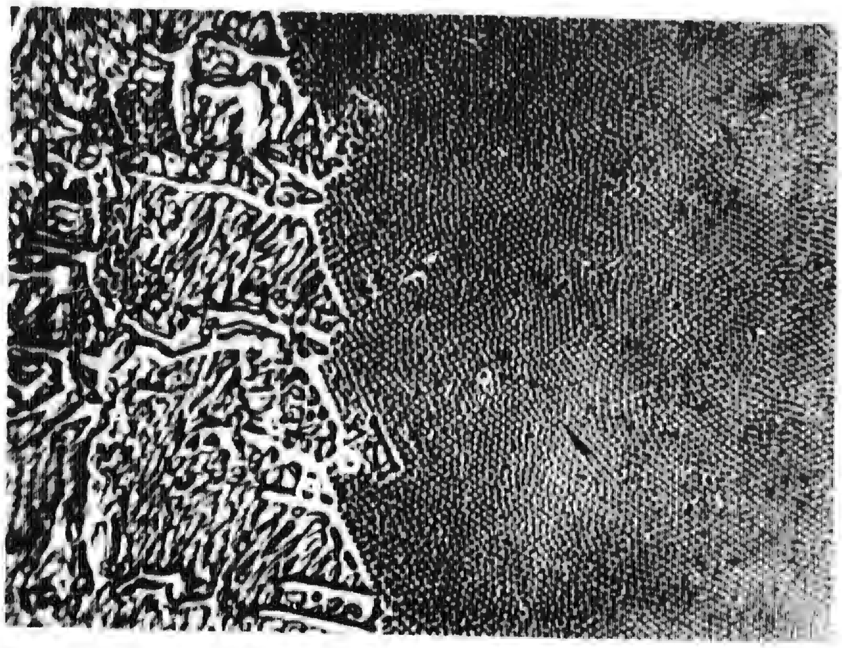

Figure 3. Rod colony with three-vaned dendritic boundary; X 1200. Note how dendrite vanes bound area.

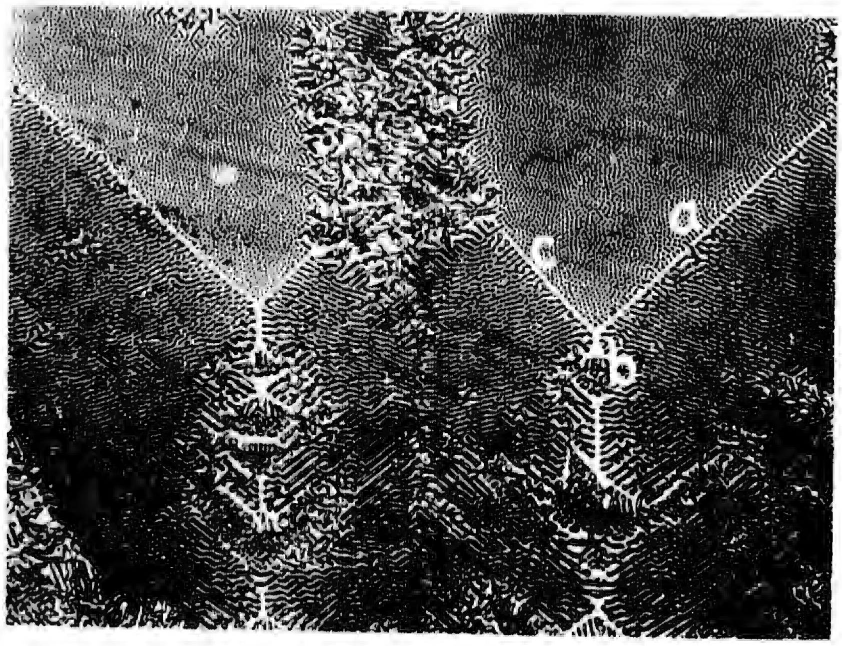

Figure 4. Three-vaned dendrites with associated rod and lamellar colonies; X 220. Transverse section of a 3.2% magnesium alloy grown at 3.75 cm./hr., etched with nital

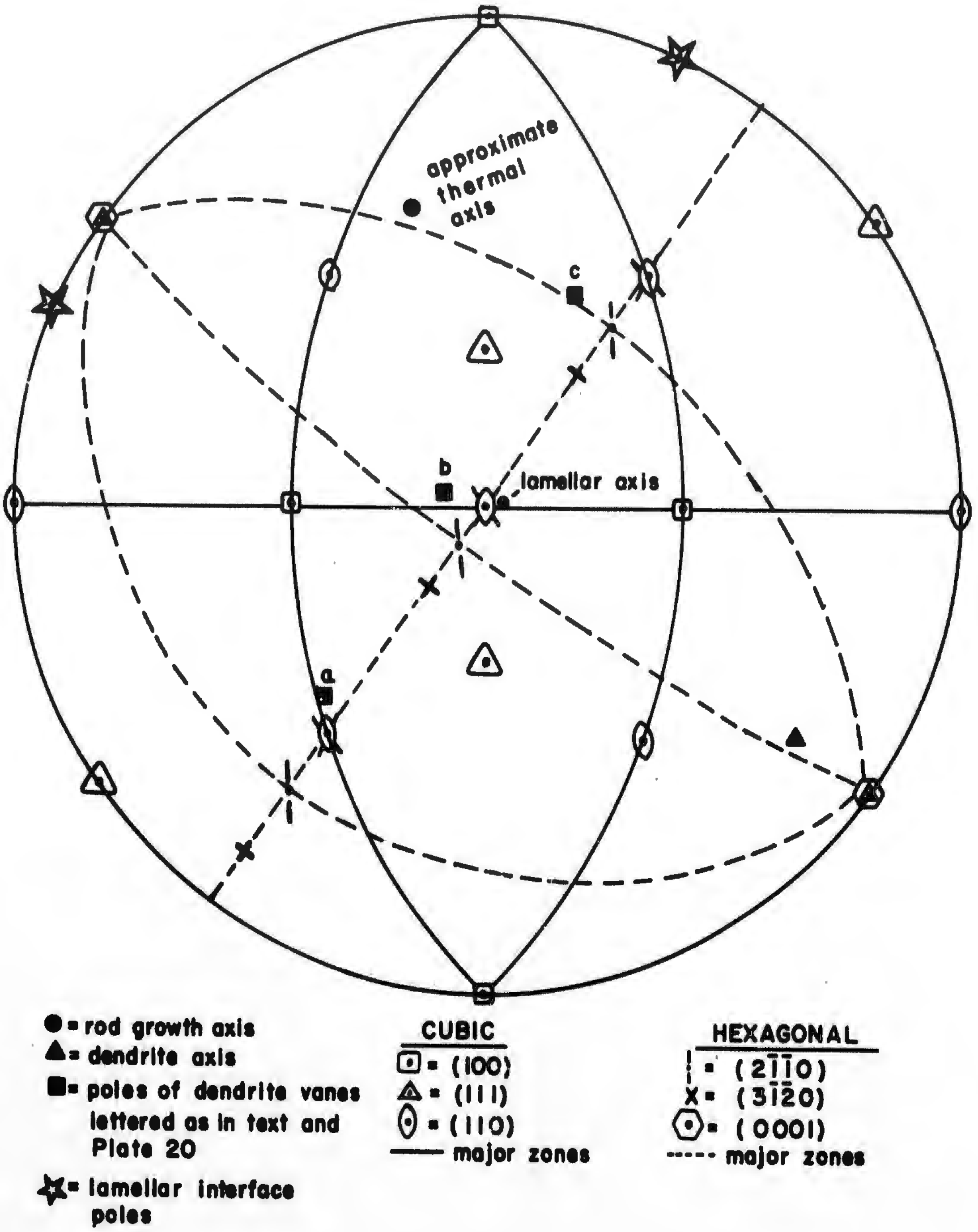

Figure 5. Stereogram showing orientation relation between three-vaned dendrites and associated rods, and lamellae: same specimen as figure 4.

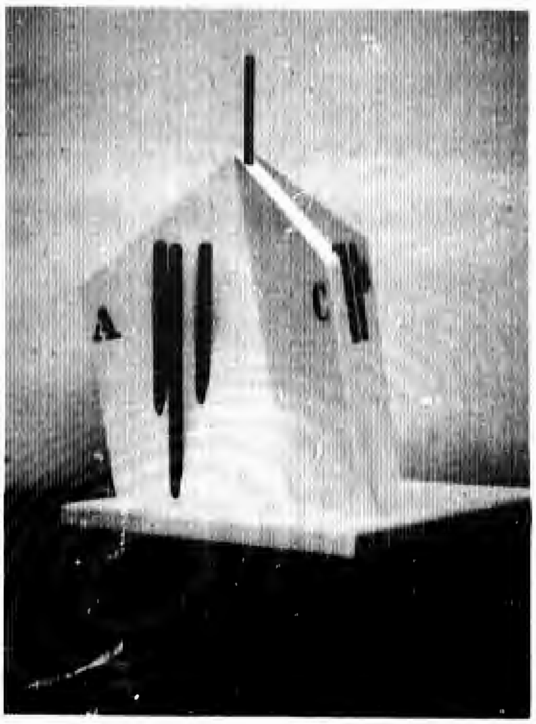

Figure 6. Model showing cooperative growth of rods (on vane A), lamellae (on vane B), and a three-vaned dendrite. The thermal axis is shown by a small rod near the dendrite tip; the resulting microstructure is seen in figure 4.

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The $Zn-Mg_2Zn_{11}$ eutectic can solidify in several different morphologies, all of which have the same general crystallographic orientation relationship. This relationship combines with the preferred growth direction and the rate and direction of heat flow to determine which morphology will predominate.

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