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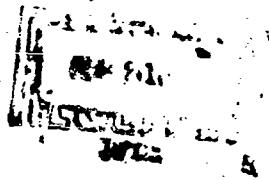
THE STRUCTURE OF ALUMINUM-SILICON ALLOYS

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FC

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ABSTRACT

The microstructures and the morphologies of the phases of unmodified Al-Si alloys have been examined through the use of special etchants and a chemical extraction technique. X-ray diffraction studies have been used to confirm the metallographic observations. Although the dendritic form of the primary α phase was found to be unaltered by changes in the growth conditions, the form of the primary Si phase was not unaffected by these changes. The usual complex idiomorphic form of the Si phase was transformed to the dendritic form when growth occurred in a super-saturated liquid. Eutectic Si plates, which have been observed to grow from primary Si particles, dominate the eutectic transformation and, by branching, restrict the growth of the eutectic α phase. This mode of solidification produces fine eutectic colonies in this abnormal eutectic structure.

PROBLEM STATUS

This report completes one phase of the problem; work on other phases is continuing.

AUTHORIZATION

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THE STRUCTURE OF ALUMINUM-SILICON ALLOYS

INTRODUCTION

Aluminum and silicon form a simple eutectic system, the eutectic occurring at 577.2°C with a composition of 12.7 w/o Si (1). The two terminal solid solutions are α , the aluminum-rich phase which may contain as much as 1.5 w/o Si in solution, and Si, which can accommodate very little aluminum. Since this second phase is essentially pure silicon, the chemical symbol of the component has been retained as the phase designation. Although the constitution of this system is uncomplicated, the solidification characteristics of its alloys are complex. The eutectic structure, lacking any apparent order in the arrangement of the two constituent phases, has been set apart from other eutectics as abnormal or anomalous. The structures of the binary Al-Si alloys are greatly altered by changes in the solidification conditions and are transformed into an entirely different form by the modifying effect of trace amounts of sodium. The unmodified alloys of this system are usually called normal even though they contain the abnormal eutectic structure.

The literature contains a large number of reports on the solidification characteristics of the normal (unmodified) and modified Al-Si alloys. The primary evidence in these studies is always derived from metallographic examinations. (Even thermal data require metallographic justification.) This metallographic evidence has always been collected from the examination of essentially unetched sections of the alloys since the usual etchants, mixed acid solutions containing HF, only clean the surface and outline the Si phase by attack. Thus, these observations are limited to the populations, sizes, and shapes of the Si particles as displayed in the metallographic section. Admittedly the changes in growth form of the individual crystals can be used to evaluate changes in the growth conditions, but the limited view provided by the random plane of metallography imposes a severe restriction on the observer. A few examinations of the forms of extracted Si particles have been reported, but in these no detailed study of the solidification process was pursued. Thus, the observations of the structures of these Al-Si alloys are limited, and the proposed mechanisms of solidification derived from these suffer accordingly.

In the current studies of the solidification of normal and modified Al-Si alloys a variety of techniques have been used to examine the structure and morphology of the phases in detail. These include visual and x-ray examinations of chemically extracted phase-particles, deep electrolytic etching to correlate the observations from extracted particles with metallographic data, the use of a modified CP-4 etchant to show structural details in the Si phase, and an anodizing treatment to define the grain size and relative orientations of the α phase.

This report describes these techniques and summarizes the significant observations afforded by their application to normal (unmodified) Al-Si alloys. Since these were developed and applied to experimental specimens for the purpose of gaining an understanding of the solidification process, it is natural that the interpretation of these observations in this report will involve some discussion of the solidification of the alloys. However, many of the aspects of the solidification process in unmodified Al-Si alloys will be reserved for a separate report. Similarly, the observations from modified alloys and a detailed discussion of the solidification of these alloys will be the subject of subsequent reports.

TECHNIQUES

In the following discussion of the techniques used in the examination of the structures and morphologies of the phases, examples are cited from among the figures of the body of the report to illustrate the effectiveness of each technique.

Chemical Extraction

Particles of the Si phase were extracted from the alloys simply by dissolving the α matrix in dilute hydrochloric acid (25 to 35 v/o HCl (37%) in water). Other investigators have used more dilute solutions of HCl (2) or an electrolytic method employing HCl as the electrolyte (3). Previously (4) it had been established that prolonged exposure of the extracted Si particles to the acid solution caused no perceptible alteration of the fine surface structure of these particles, e.g., the structures in Figs. 2c and 2d were unaltered after 72 hours exposure to a 35 v/o HCl solution. Thus, in the observations of extracted Si, the surface detail of all particles is considered to be a true representation of the surface of the particle in the alloy. The more massive idiomorphic primary silicon particles, undamaged in the extraction, are probably complete particles, but the thin eutectic plates are only portions of these particles. These fine eutectic Si particles, although not attacked by the acid, are quite easily fragmented during extraction, washing, or handling during examination.

Since the acid solution preferentially and rapidly attacks the matrix at the α :Si interfaces, dendritic primary α particles were frequently released from the dissolving alloy. These particles had been thinned by the acid attack, but the true form of the dendrite was retained and provided confirmation of the form deduced from metallographic observations.

Anodizing

The extraction process provided specimens of primary and eutectic Si as well as primary α dendrites but destroyed the eutectic γ phase. To examine this latter phase the anodizing process developed by Kone and Pearson (5) was applied to metallographic specimens. Using their solution A (350 cc orthophosphoric acid (85%), 132.5 cc diethylene glycolmonoethyl ether, 5 cc HF (48%), and 12.5 cc water) and maintaining a 20 to 25 volt potential across the cell by adjusting the current during the anodizing treatment, satisfactory films were produced on very carefully polished samples of these two-phase alloys. Three to five minutes were required to produce the desired films in the well-stirred, room-temperature anodizing bath. The microstructures of the anodized alloys showed no pitting at the α :Si interfaces - the use of any conventional aluminum grain size etch leads to prohibitive pitting at these sites. The removal of aluminum from the specimen surface in the formation of the film left the Si particles in slight relief and made visible a large number of the α grain boundaries. When viewed under polarized light, the size and relative orientations of the α grains were clearly defined by the anodic film.

The effectiveness of this type electrolytic etchant is demonstrated by the series of photomicrographs shown as Fig. 9. The change in the grain contrast with the angular setting of the specimen relative to the polarized light beam is quite clearly displayed in these. Other examples, showing the α grain size in these alloys, are presented as Figs. 8, 12, and 14.

CP-4 Etchant

The structure of the Si phase was revealed by etching metallographic specimens of the alloys and sections of extracted silicon particles with a modified CP-4 etching solution

(one part HF (48%), two parts HNO₃ (70%), and ten to fifteen parts glacial acetic acid). The rate of attack of the standard CP-4 solution was much too rapid, causing the removal of fine eutectic Si from the microstructure in etching times as short as 10 seconds. By increasing the acetic acid content of the standard solution, the rate of attack was diminished (etching times up to 60 seconds) and the nature of the action of the etch appeared to be modified. Other solutions recommended for etching pure aluminum or pure silicon were investigated, but these generally produced severe pitting at the α :Si interfaces or such coarse pitting of the fine Si particles that all structural detail was obliterated.

The modified CP-4 etchant used in this study revealed grain and twin boundaries by attack and produced some evidence of the growth structure of the particles by straining (see Figs. 3 and 5). The patterns of boundaries and stains produced by this etchant were representative of the structure of the Si particles and were not unduly sensitive to the preparation of the section surface. This was demonstrated by observing the etching characteristics of a series of sections through the thickness of several extracted Si particles which had been vacuum impregnated with and mounted in an epoxy resin; the etch pattern on each particle retained the same form on all sections.

These stain patterns were highly colored, the colors being caused by interference films. As a consequence of this, the coloration and contrast in the stain pattern was a function of etching time. Overetching caused the film to become thick and the contrast in the pattern to decrease; the thickest sections of the film became opaque and granular or reticulated. Regardless of the etching time, the basic pattern of the stain remained the same. The stain pattern, the result of local variations in the rate of film formation, appears to be associated with the local variations in the impurity content of the silicon. To verify this observation small rods of vapor-grown semiconductor silicon were inserted into a molten sample of a 14 w/o Si alloy, held at 600°C, and the melt was allowed to solidify. The rods of silicon with a surface deposit of primary Si crystals from the alloy were extracted, mounted in Epon, sectioned, and examined metallographically. Observation of the specimen after etching for different lengths of time showed the following development of the stain pattern:

10-second etch - The surface Si particles grown from the melt showed a strong stain pattern very similar to those observed on other primary Si particles. The vapor-grown substrate was unaffected by the etch.

20-second etch - The stain on the surface particles had become very dark (overetched). Portions of the substrate near the surface not covered by regrown Si showed a light stain. The central portion of the substrate was unaffected.

80-second etch - Surface particles were nearly black, and the regions of the substrate, which showed a light stain at 20 seconds, were now very dark. The boundaries between these regions and the central portion were very sharply defined because of the overetching. The central region, completely free of any detectable film, showed lines of small well-developed etch pits.

Film formation during etching is thus associated with the presence of aluminum in the silicon (aluminum which is incorporated during the growth of the primary Si crystals deposited from the liquid alloy and by its solid-state diffusion into the substrate).

Although the numerical results of several different determinations of the solubility of aluminum in silicon are somewhat in disagreement (6,7), they do agree that the solubility of aluminum decreases continuously with lowering temperature from about 1100°C. Between 700° and 577°C, the temperature range in which primary Si precipitation occurs in the experimental alloy, the solubility of aluminum in silicon is reduced by a factor of two. These solubility data can be correlated with stain patterns observed on the Si particles in Al-Si alloys. In general, the staining developed first and most rapidly in the

central portion of the primary particles, i.e., the portion of the particle deposited at the highest temperature and therefore, the region containing the greatest concentration of aluminum (see Fig. 5). In order to obtain contrast in the pattern on the eutectic Si particles of an alloy, it was frequently necessary to lengthen the etching time and thus, over-etch the primary Si particles. From the equilibrium concentrations of the phase diagram, the eutectic Si particles should contain less dissolved aluminum than the bulk of the primary crystals, and thus, the observed etching behavior tends to support the dependence of the etching rate on the aluminum content of the Si. In some primary Si particles, as in Fig. 3, the etchant revealed evidence of growth layers. This layer pattern is probably associated with fluctuations in the surface concentrations during growth. In other particles, Fig. 5, a dendritic growth pattern was shown by this same effect.

Deep Electrolytic Etch

The standard Knuth-Winterfeldt electrolyte (1 part perchloric acid, sp gr 1.20; 7 parts ethyl alcohol; and 2 parts glycerine) was used with the Disa-Electropol to remove a thick layer of the σ matrix and expose the Si particles in the metallographic section of these alloys. These deeply etched structures provided a means for correlating the microstructural observations with those derived from the extracted particles.

X-Ray Examination

Laue back-reflection patterns were used to define the growth forms of extracted primary σ and Si particles. They were also utilized to confirm the evidence of twinning in Si and the fine grain size of the eutectic σ both being revealed by the special etchants.

PHASE MORPHOLOGY

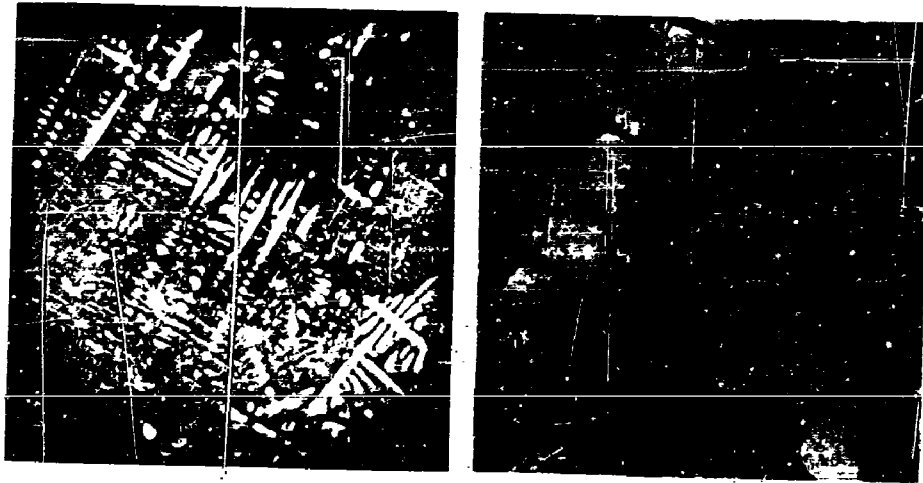
Primary σ

Primary σ always develops a characteristic dendritic form. The crystallographic aspects of the dendrite can be deduced from metallographic observations alone, but the extracted σ dendrites permitted completely unambiguous observations. The dendrites are formed by growth along three mutually perpendicular axes. Laue patterns showed that these are $\langle 100 \rangle$ and that the dendrites are single crystals.

The form of the primary σ crystal does not change with different growth conditions. All alloys containing less than the eutectic concentration of silicon, whether slowly cooled or quenched, always show dendritic primary σ . The spacing of the arms and the extent of growth is naturally altered by changes in the cooling rate and concentration, but the form remains unchanged.

The difficulty of nucleating primary σ in the supersaturated liquid of these hypoeutectic alloys has been demonstrated in the data for the liquidus determination (1). From the examination of the microstructures of a number of slowly cooled and quenched specimens, it has been concluded that the nucleation of primary σ in a homogeneous liquid specimen occurs almost exclusively at the specimen surface and that nucleation within the liquid is very improbable. The microstructure of an 11.4 w/o Si alloy specimen, which had been slowly cooled to 577.5°C, held isothermally for 60 minutes, and then quenched, is shown in Figs. 1a and 1b. Although this specimen has been held at a temperature 8.5°C below the liquidus, very few primary σ dendrites were formed and the aluminum supersaturation of the liquid was not eliminated. On quenching, the fine σ dendrites formed; almost all of these grew from the surfaces of the existing coarse σ dendrites taking their orientations from these and showing the same form. These observations, clearly presented

in the structure of Fig. 1, were confirmed by the examinations of this type structure with polarized light after anodizing. With but few exceptions, the dendrites, which formed on quenching, showed the same orientation as the coarse dendrites formed during the isothermal period. The few exceptions were probably nucleated at the specimen surface or grew from coarse dendrites which were not exposed in the metallographic section.



(a) 16X

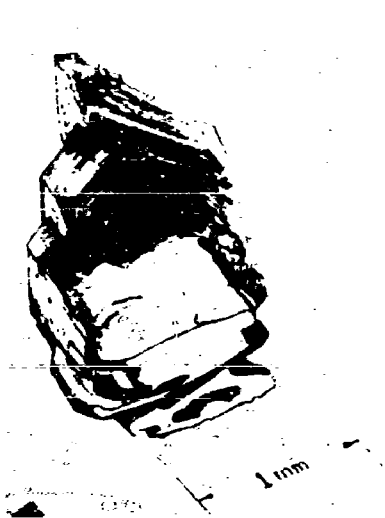
(b) 90X

Fig. 1. Primary α dendrites in a specimen of an 11.4 w/o Si alloy, specimen equilibrated at 577.5°C for 60 minutes before quenching, Keller's etch*

Primary Si

Unlike the primary α phase, the primary Si phase cannot be characterized by a simple form. Obinata and Komatsu (3) have described the primary Si particles as aggregates or twinned crystals which usually exhibit a platy form. The general term applied to the forms of these particles is idiomorphic. This term, because it is so general, is probably more representative. Primary Si particles extracted from a slowly cooled alloy are rather massive, angular particles of complex form frequently showing a tendency toward the platy form. Sketches of a portion of one of the simpler particles are shown in Figs. 2a and 2b. This particle was extracted from a metallographic sample which had been etched with the modified CP-4 reagent. White areas in the sketches are the sections which appeared in the metallographic specimen and the pattern of lines in these areas represent the boundaries defined by the etchant. These sketches, showing the idiomorphic character of the particle and its tendency toward the platy form, also, clearly illustrate the impossibility of deducing the true form of the particle from the section observed in the microstructure. The complexity of the form of the section of silicon particles grown in slowly cooled alloys is shown in Figs. 5 and 13.

*All photographs have been reduced approximately 20 percent in printing unless otherwise indicated. The original magnification is shown under each figure.



(a) Sketch, perspective of particle, 35X



(b) Sketch, plan, 70X



(c) Photographs of surface detail, 250X. (Reduced approximately 41%.)



(d) Photographs of surface detail, 250X. (Reduced approximately 41%.)

Fig. 2 - Extracted idiomorphic primary Si

The study of the shapes of primary Si particles was further complicated by the effect of the conditions of solidification on the growth form. Primary Si particles extracted from slowly cooled, small specimens were usually idiomorphic in form. Their forms were comparable with that of the particle of Fig. 2, and, in section, they showed evidence of twinning and layer growth of the type illustrated in Figs. 3 and 4. The primary Si particles extracted from a large furnace-cooled ingot were much more complex and showed evidence of dendritic growth. A section of one of these particles, mounted in an epoxy resin and etched with the modified CP-4 solution, is shown in Fig. 5. In addition to the usual stain pattern and the lines which are presumably twin boundaries, some portions of this section show stain patterns which are suggestive of dendritic growth. Since the epoxy mount is transparent, portions of the complex surface structure of this particle can be seen below the plane of polish. Other primary Si particles from this alloy were completely devoid of the usual massive crystal form and appeared in the microstructure as striking dendrites. Examples of this form are shown in Fig. 6. The specimen of Fig. 6a was subjected to a prolonged electrolytic etch to show the difference in the orientations of the Si plates of the dendrite relative to the plane of polish. Figure 6b is a section through another of these particles which was extracted and mounted in an epoxy resin. In these sections the very regular platelike structure of the dendrite is almost completely enclosed by plates of irregular outline. Because of this, the external surfaces of the extracted dendritic particles reveal none of the simplicity of structure observed in the section. The surface plates of Si as shown in Fig. 7 were frequently covered with rather regular arrays of small crystallites. The surface shown on the left (Fig. 7a) might well be a {111} plane that has developed small platelike crystallites bounded by {111} planes.



Fig. 3 - Section of an extracted idiomorphic primary Si particle showing twinning, layer growth, and eutectic Si particles growing from the primary surfaces, etched with modified CP-4, 300X



Fig. 4 - Primary and eutectic Si particles, etched with modified CP-4, 500X

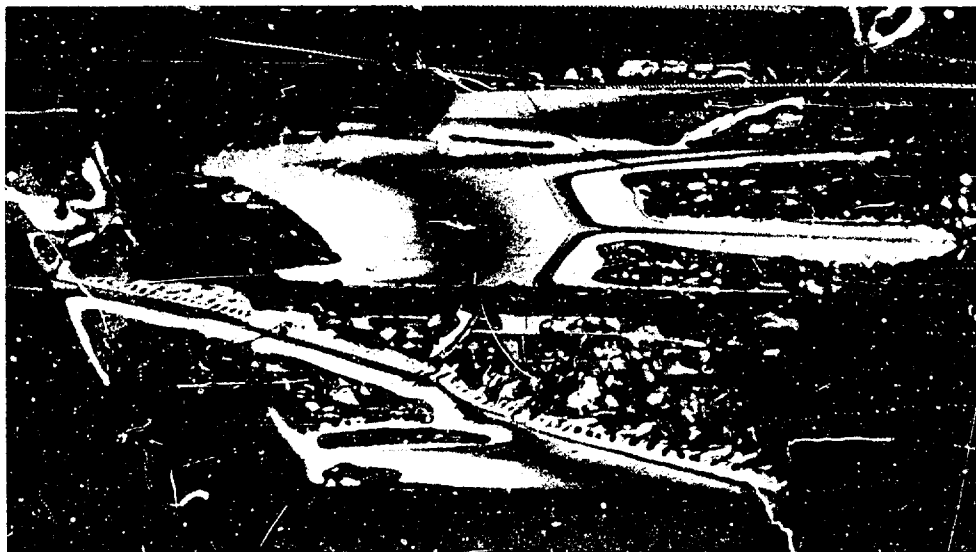


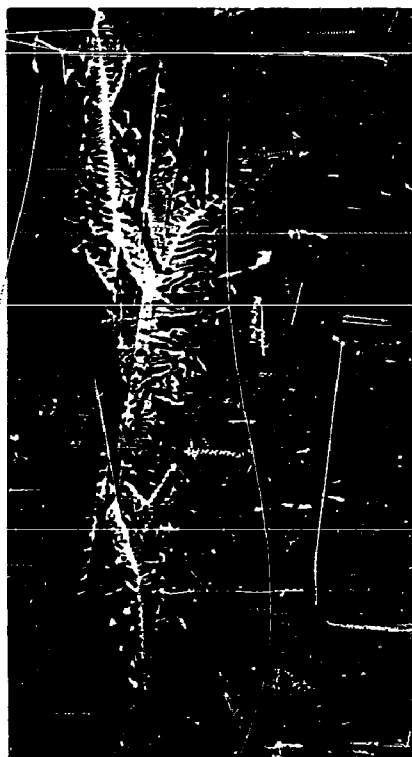
Fig. 5 - Extracted primary Si showing twinning and a dendritic growth pattern, etched with modified CP-4, 100X

That shown on the right (Fig. 7b) may be a $\{100\}$ plane with ridges in the $\langle 110 \rangle$ direction. From these ridges have grown perfectly formed, tiny tetrahedra each bounded by $\{111\}$ planes.

While the complex idiomorph is the form most often associated with the primary Si phase, these dendrites of Si are another form of this primary phase. A few investigators have observed this dendritic form of Si and reported this finding. Spengler (8) classified the dendrite as one of three eutectic forms. Gärtler (9) and Scheil and Zimmermann (10) have concluded that it is a form of the primary Si phase. Scheil and Zimmermann based their classification on the high proportion of Si in the structure, i.e., about 20 to 25 v/o. Though observed, and correctly classified as primary Si, no explanation has been offered to account for the change from the usual idiomorph to this dendritic form.



(a) Deep electrolytic etch, 200X



(b) Section of an extracted particle, unetched, 75X

Fig. 6 - Dendritic primary Si from a slowly cooled ingot

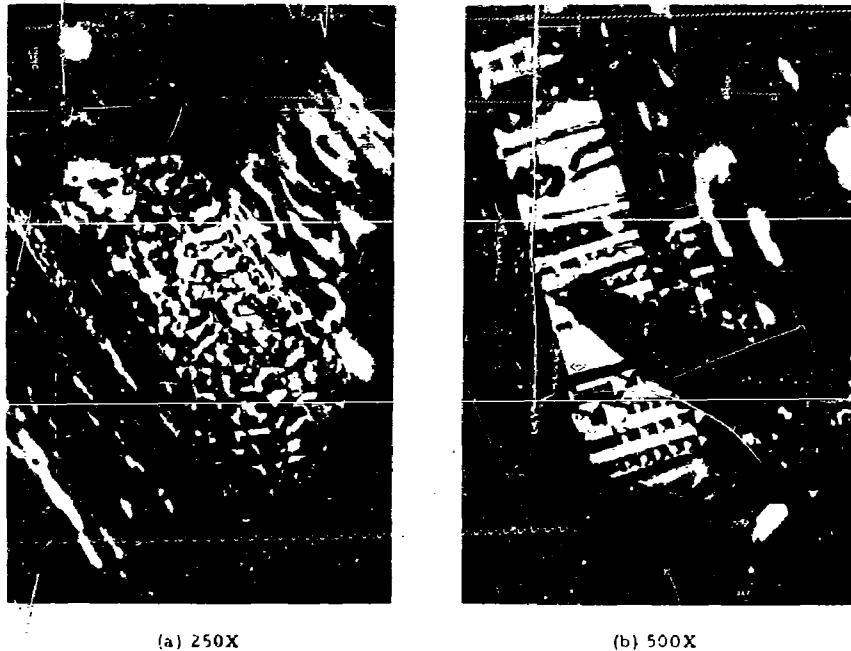
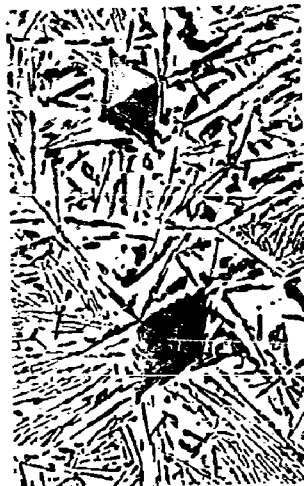
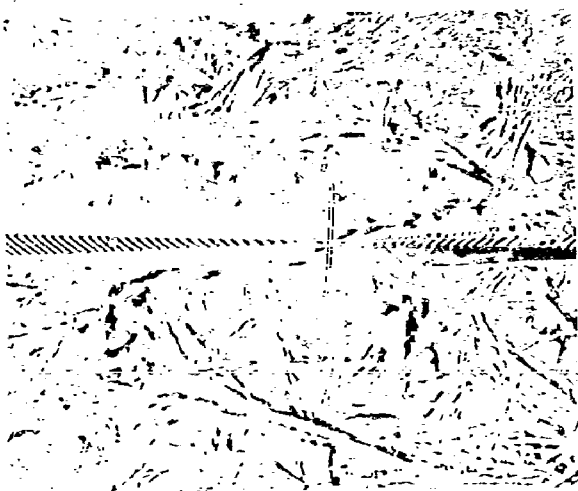


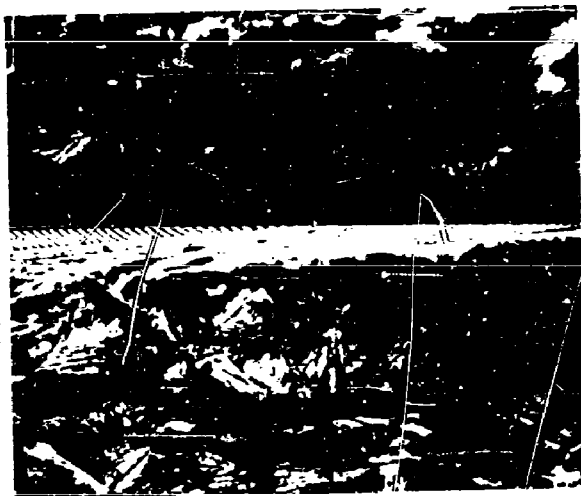
Fig. 7 - Surface structure of the external plates on extracted Si dendrites

The general conditions for the formation of dendrites require the growth to occur into a solution of relatively high supersaturation, usually along a low thermal gradient. Since the surface of the Al-Si alloys affords excellent sites for the heterogeneous nucleation of Si, very little supersaturation can be achieved in small samples without employing very rapid cooling rates. The surface-nucleated Si particles are always idiomorphic. Some small, poorly developed dendrites of Si were found in the interior of the quenched samples used in the phase diagram work, but only idiomorphs were found in the slowly cooled specimens and most of these were located at the specimen surface (1). In the larger specimen, as a consequence of the geometry, regions of high silicon supersaturation occurred in the body of the liquid and dendritic primary Si particles grew in these regions.

Conditions for extensive dendritic Si growth were achieved in the zone melting of long thin rods of a 13 w/o Si alloy specimen. Long thin dendrites of Si grew parallel to the axis of the bar, i.e., roughly perpendicular to the solidification interface. Sections of these are shown in the microstructures of Figs. 8 and 9. These figures present longitudinal and transverse sections of one specimen which was solidified at a rate of 1 mm/minute with a thermal gradient of about 5° to $6^{\circ}\text{C}/\text{mm}$ at the interface. Very similar structures were obtained using growth rates of 1.0 to 3.8 mm/minute and gradients of 4° to $6^{\circ}\text{C}/\text{mm}$. In all of these specimens a few small idiomorphic Si particles were observed at the surfaces of the bar, but, within the body of the specimen, all of the primary Si was dendritic. When the maximum temperature in the liquid zone was only slightly above the liquidus of the alloy and the rate of growth was high, a nonhomogeneous liquid phase was formed. The inhomogeneity may have been regions of high silicon concentration in the liquid or even incompletely dissolved Si crystals. The structure of the zone-melted alloy formed under these conditions contained a large number of small



(a) Anodized, bright field illumination, 100X



(b) Anodized, polarized light, 100X

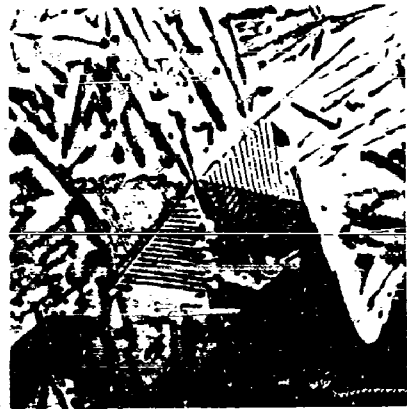
Longitudinal

Transverse

Fig. 8 - Longitudinal and transverse sections of a zone-melted 13 w/o Si alloy specimen showing dendritic primary Si



(a) 0 degrees



(b) 65 degrees



(c) 120 degrees

Fig. 9 - Transverse section of a Si dendrite in a zone-melted specimen, analyzed, polarized light, relative rotation of metallograph stage, 200X

idiomorphic Si particles and no dendrites. Since this liquid contained a large number of sites for the precipitation of Si, the degree of supersaturation required for the growth of dendrites could not be attained and the primary Si grew as idiomorphs.

From these observations it is clear that the dendritic Si is indeed a form of the primary Si phase. The high proportion of Si in this structure, as noted by Scheil and Zimmermann (10), eliminates from consideration any proposal of a displacement of the apparent eutectic composition attributed to an increasing cooling rate. The demonstration, that altering the growth conditions of the alloy can entirely replace the idiomorphic form by the dendritic form, shows that these are both forms of the primary Si phase.

The fact that dendritic primary Si was not reported until relatively recently is probably directly assignable to the impurity content of the alloys used in earlier studies and those of commerce. When sites for the heterogeneous nucleation of primary Si are available in the liquid, the required supersaturation for dendritic growth is not easily attained.

Crystallographic characteristics of the primary Si particles were determined from Laue back-reflection photographs. The complexity and diversity of the forms of the primary Si made it impractical to analyze any of these forms completely, but several common characteristics were defined. In most cases the Laue patterns from idiomorphic particles indicated that these were single crystals, but, as the etched sections have shown, these were often twinned. Obinata and Komatsu (3) have proposed that the surfaces of these idiomorphs were made up of {111} planes alone. The x-ray patterns and the observed geometry of these crystals indicated an extensive development of {111} surfaces but appeared to allow for some {110} and {211} surfaces. When the idiomorphs were of a more tabular form, as in Fig. 2, the most prominent surface was a {111} surface and the longest dimension of the plate was along a <211> direction of this surface. This direction of rapid growth agrees with the findings of Billig (11) on the preferred growth direction of germanium in the melt. When an extracted Si crystal was rotated 90 degrees from the {111} surface about the <211> axis the Laue pattern revealed twinning of the type defined by Ellis and Treuting (12). This twinning, very common in diamond cubic materials is shown in the diagrams of Fig. 10. Geometrically it is depicted as a 70 deg 32 min rotation about the [110] direction to bring the [112] into coincidence with the original [112], or the ($\bar{1}\bar{1}\bar{1}$) to the original (111). The distribution of the major poles in the two Laue patterns taken at 90 degrees to one another is indicated in the lower drawing of this figure.

The diffraction patterns from extracted dendritic primary Si particles were complicated by diffraction from the eutectic Si plates which were always attached to the primary structure. Because of the size and fragility of the dendrites, it was not possible to remove these eutectic particles from the dendrites. As a result, the Laue pattern contained many rather randomly distributed spots from these eutectic plates which complicated the interpretation of many of the patterns. Amid this profusion of random Laue spots a number of zones were found indicating single crystals of very similar orientations. This pattern is interpreted as originating in the plates of the Si dendrite. These zones showed that the plates exhibit the same characteristics as the idiomorphic Si, i.e., the plates of the dendrites are probably bounded by {111} planes and the long axis of the dendrite is probably parallel to a <211> direction.

Eutectic Si:

The basic form of the eutectic Si particle is a thin plate. Even in slowly cooled specimens, these plates are so thin that extracted specimens frequently appear red-brown by transmitted light. These particles grow into extensive nonplanar arrays of interconnected plates, but, because of the fragility of these thin plate structures, the extracted specimens are only fragments of the original particles. Photographs of a few rather planar particles, representing only a few of the myriad forms found among the extracted eutectic

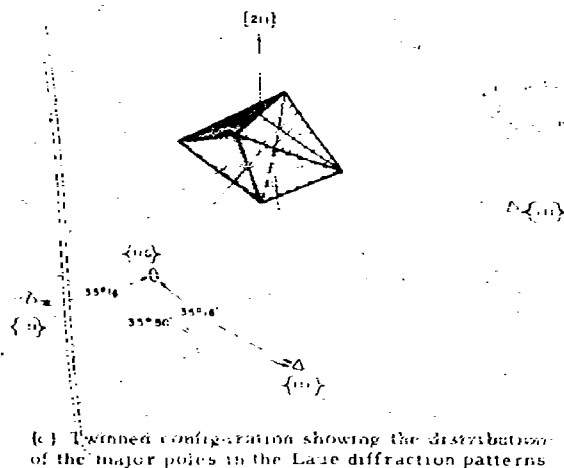
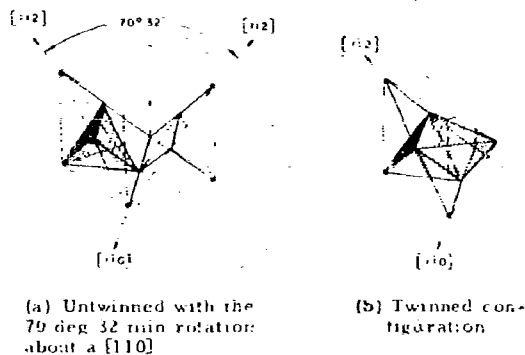
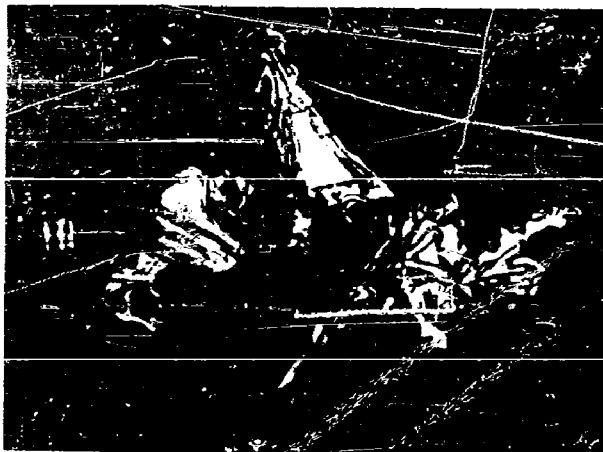


Fig. 10 - Twinning in diamond cubic Si

Si, are shown in Fig. 11. Other examples may be found in the paper by Rhines and Timpe (2). The particles shown here are representative but, by selection, oversimplified. These were selected because they were simple, and, being relatively flat, the surface detail could be photographed. These particles, or fragments of particles, show an angular form and a surface growth structure which is very similar to that observed on portions of the idiomorph of Fig. 2.

When etched, sections of the eutectic Si particles show some of the same characteristics as the idiomorphic primary particles. This similarity is illustrated in Fig. 4 and also in Fig. 3. The striations in the eutectic particles are probably evidence of twinning. The particles growing from the twinned surface of the extracted primary Si idiomorph shown in Fig. 3 contain the same twin boundaries as the substrate. In these figures and in Fig. 13, the dependence of the orientation of the eutectic plates on the orientation of the primary particle may be detected in the distribution of the eutectic particles about the different faces of the idiomorph. Similarly, the eutectic plates around the dendritic primary Si frequently show this orientation dependence. In fact, it is difficult to decide where the boundary between the primary and eutectic structures should be drawn in the examples



(a) 100X



(b) 200X



(c) 75X



(d) 220X

Fig. 11 - Extracted fragments of eutectic Si plates

of Fig. 6. These observations indicate that primary Si particles do serve as nucleating sites for the initiation of the eutectic transformation.

Eutectic α

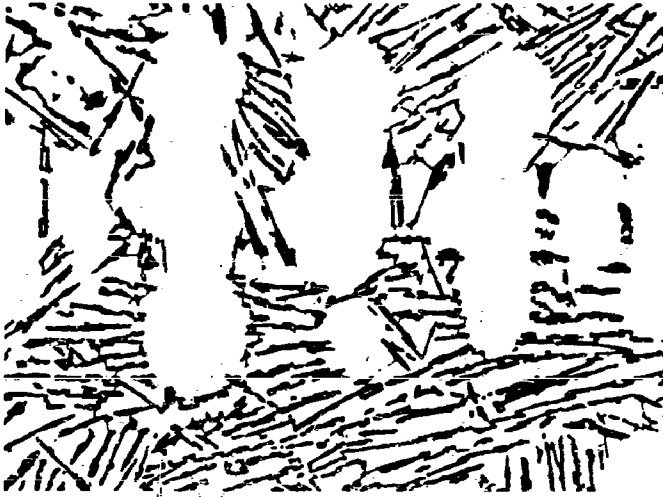
The α phase forms the matrix of the eutectic structure and, as a consequence, cannot display any characteristics of its growth through an external form. The successful application of an anodizing treatment to metallographic specimens has now provided a means of detecting the grain size and the relative orientations of the α phase in the eutectic structure.

The structure of a slowly cooled 10 w/o Si alloy sample is shown in Fig. 12. Both photomicrographs were taken after the specimen had been anodized and show the distribution of eutectic Si particles around a section of a primary α dendrite. In the upper print, taken with bright field illumination, the individual Si particles and some of the grain boundaries in the α phase are clearly defined. Although the boundaries are somewhat weakly delineated in a few areas of the print, it is possible to detect grain boundaries separating the primary α from the eutectic α . The same area, photographed with polarized illumination, is shown in the lower print. The uniform tone of all of the dendrite arms is cited as proof that the anodizing treatment does produce uniform films on grains of the same orientation. The strong difference in tone between the primary α dendrite and the surrounding eutectic α grains and the existence of an interface separating these is proof that the eutectic α does not form by the continued growth of the primary crystal.

A closer examination of this structure shows that the Si plates contained within individual eutectic α grains tend to be parallel. Some apparent exceptions are found in the prints but many of these can be resolved during visual examination by rotating the specimen relative to the polarized light beam. For example, within the very dark grain in the lower right corner of the print (Fig. 12b) some of the Si plates appear not to be parallel but almost perpendicular. A rotation of the specimen showed that this was not a single α grain but really three grains. Some of the boundaries separating these grains can be seen in the upper print. Thus, for any fixed setting of the polarizer, analyzer, and angular position of the metallograph stage, all of the α grains are not shown with equal contrast. The apparent grain size in any photograph is larger than the actual grain size. This limitation of the etchant is demonstrated in the series of photomicrographs of Fig. 9.

Recognizing this effect and the resulting inability of a photomicrograph to show all of the detail of the structure, several specimens were carefully examined on the metallograph. The distribution of eutectic Si about a primary particle in a 13 w/o Si alloy specimen is shown in Fig. 13. The upper print is a photomicrograph of the anodized specimen taken with bright field illumination. In it a number of the most prominent α grain boundaries are visible. From direct observations of this area with both bright field and polarized illumination, a more complete record of the α grain boundary net was obtained and inked in for emphasis (see Fig. 13b). In this structure the long parallel Si plates are imbedded in large grains of α ; the more randomly arranged plates are enclosed by much smaller grains of α . As before, the Si plates within a single eutectic α grain are generally of one orientation.

Similarly, the random arrangement of the Si plates of the structure shown in Fig. 14 become more orderly when the eutectic α grains were revealed by anodizing and viewing in polarized light. This figure is representative of the eutectic portions of the structure in a slowly cooled sample of a 14 w/o Si alloy. The corrugated Si plate which extends across the center of this print is of particular interest. This plate may be of eutectic origin or it may be part of a poorly developed primary Si dendrite. In either event, its form and length indicate that it was one of the first members of the present population. Along the upper face of this plate a number of distinct eutectic α grains are found. The α

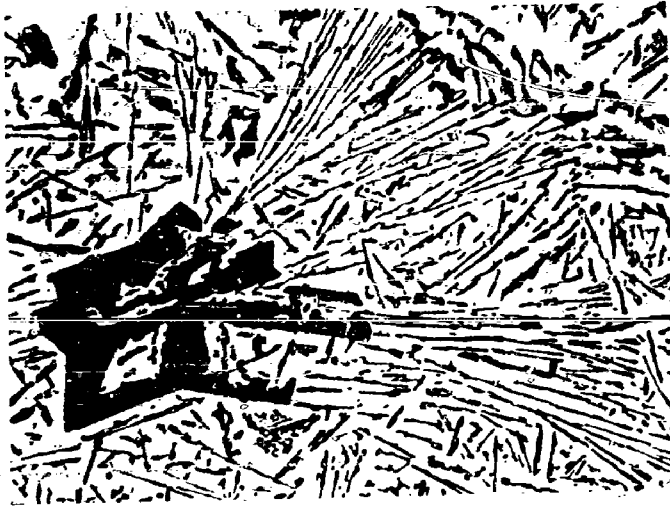


(a) Anodized, bright field illumination, 250X



(b) Anodized, polarized light, 250X

Fig. 12 - Distribution of eutectic Si and α grains around a section of a primary α dendrite in a 10 w/o Si alloy specimen



(a) Anodized, bright field illumination, 200X



(b) Same as 13a, with α grain boundaries emphasized

Fig. 13 - Distribution of eutectic Si and α grains around a section of a primary Si particle in a 13 w/o Si alloy specimen



Fig. 14 - Eutectic structure in a 14 w/o Si alloy specimen, anodized, polarized light, 100X

below the corrugated plate appears to be a single grain, but it is probably polycrystalline; however, the orientation of this grain, or these grains, is different from those above the plate. This Si plate has been singled out because it clearly illustrates these observations, but it is not unique. Throughout the structures of Figs. 12, 13, and 14 many eutectic Si plates are to be found which form part of the boundary between two α grains or extend across one or more α grains and penetrate others.

In a study of the solidification process in these alloys (13) it has been shown that the Si phase leads the concurrent α phase in the eutectic transformation. The Si plates extend beyond the eutectic solid into the liquid, and the α phase, nucleated on the eutectic Si plates, grows along these surfaces. The continued growth of the individual α grains is inhibited, often arrested, by the branching of the Si plate structure. The characteristics of the eutectic structure, which have been illustrated by the photomicrographs of Figs. 12, 13, and 14, result from this solidification process. The growth of eutectic α grains along and between parallel Si plates proceeds unimpeded, but, when the branching of the Si plates becomes extensive, the growth of the α phase is interrupted and new α grains are nucleated on the Si beyond the obstructing plates.

If a unique orientation relationship between the Si and α phases existed, the α grains on opposite sides of a Si plate would be expected to have the same orientation. However, even this normal expectation is doubtful in the Al-Si eutectic; diamond cubic Si is a polar crystal and the (111) and ($\bar{1}\bar{1}\bar{1}$) planes are not equivalent. If the two sites of α nucleation are on different branches of the same Si crystal, the relative orientations of the two α grains would not be the same for the most general type of orientation relation between the Si and α . In the more restricted growth conditions of the precipitation of Si from super-saturated α , not one, but five possible orientation relationships have been reported (14).

Back-reflection Laue patterns from metallographic specimens show rather complete Debye rings for both eutectic phases. These patterns confirm the fine grain size of the eutectic α revealed by the anodizing etch but show no evidence of a preferred orientation of this phase. Even in the zone-melted specimens, the α grains show this randomness of

orientations. The lack of a growth texture in the σ phase of these directionally solidified specimens is supporting evidence that the Si, and not the σ phase, determines the eutectic structure.

The structure shown in the series of photographs of Fig. 9 appears to contain some suggestion of a preferred orientation between the σ and Si phases. This structure is from a transverse section of the zone-melted specimen of Fig. 8. With the exception of the lower sector of the plate structure, the σ phase in each sector passed from maximum to minimum and back to maximum brilliance at 0, 90, and 180 degrees rotation of the stage. The peak intensity values were not sharply defined, and, as a result, an uncertainty of ± 10 degrees must be accepted in the angular rotation readings. As demonstrated in the sequence of these photomicrographs, three of the four sectors appear to show orientation differences of about 60 degrees. The anomalous behavior of the fourth sector, the uncertainty in the determinations of the positions of maximum and minimum reflection intensities, and the lack of sufficient crystallographic data on the orientations of either the Si or σ phases make it impossible to determine the relative orientations of the phases. However, it is abundantly clear that the σ surrounding each group of parallel Si plates is a single crystal.

This metallographic and x-ray examination of the structure of the Al-Si eutectic has shown that, unlike the normal eutectics which Weart and Mack studied (15), the eutectic grain size is small in this abnormal eutectic. These authors have defined the eutectic grain as "a region in which the matrix phase is monocrystalline" and the eutectic colony as that portion of a eutectic grain displaying a characteristic grouping of the second phase particles. In the Al-Si structure of the present study the eutectic grain and colony appear to be identical. The reluctance of the σ phase to nucleate allows the Si phase to dominate the eutectic solidification process. The natural branching growth of this phase geometrically defines the region which any single σ grain can occupy and thus, produces the identity of the eutectic grain and colony in this abnormal eutectic structure.

SUMMARY

The morphologies of the phases of the normal (unmodified) Al-Si alloys have been examined through the use of a variety of techniques. A chemical extraction process provided specimens of primary and eutectic Si particles as well as primary σ dendrites for visual and x-ray examination. The adaptation of two etching procedures have permitted a detailed examination of the eutectic structure and the growth characteristics of the individual phases. The correlation of these microstructural characteristics with the forms of the extracted phase particles was facilitated by exposing the Si phase in the microstructure to a deep electrolytic etch.

The form of the primary σ particle is independent of the growth conditions and is always dendritic along $\langle 100 \rangle$ axes.

The form of the primary Si particle is not independent of the growth conditions. The usual idiomorphic particle, which is generally quite complex in structural detail, almost always displays extensive $\{111\}$ surfaces and a tendency toward preferential growth in a $\langle 211 \rangle$ direction. Metallographic evidence of twinning in these idiomorphic crystals has been confirmed by x-ray studies. Although the equilibrium growth form is idiomorphic, a dendritic character appears in this form when growth occurs into a liquid supersaturated with silicon. The conditions for the extensive growth of dendritic primary Si particles are readily achieved in zone melting.

The eutectic Si particles are not simple plates but rather complex arrays of interconnected plates. These eutectic plates have been observed to grow from sites on the surfaces of primary Si particles and, by branching, develop into the complex plate

structures. The role of the eutectic Si phase in determining the solidification process has been discussed only briefly since this is the subject of a separate report (13).

The size and relative orientations of the eutectic α grains and the matrix of the eutectic have been clearly defined by an anodizing etch. These grains, much smaller than those of a normal eutectic, do not grow from the surface of existing primary α dendrites but, instead, are nucleated on the eutectic Si plates. The branching of the Si plate structure limits the growth of these eutectic α grains.

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REFERENCES

1. Meussner, R.A., "The Aluminum-Silicon Eutectic," NRL Report 5331, June 1959
2. Rhines, F.N., and Timpe, W.F.B., *Z. Metallk.* 48:109 (1957)
3. Obinata, I., and Komatsu, N., Science Reports, Research Institutes, Tohoku University A9:107 (1957)
4. Meussner, R.A., Doctorate Thesis, Carnegie Institute of Technology, 1953
5. Hone, A., and Pearson, E.C., *Metal Progr.* 53:363 (1948)
6. Miller, R.C., and Savage, A., *J. Appl. Phys.* 27:1430 (1956)
7. Gudmundsen, R.A., and Maserjian, J., Jr., *J. Appl. Phys.* 28:1308 (1957)
8. Spengler, H., *Metall.* 9:181 (1955)
9. Gürtler, G., *Z. Metallk.* 44:503 (1953)
10. Scheil, E., and Zimmermann, R., *Z. Metallk.* 48:503 (1957)
11. Billig, E., *Proc. Roy. Soc. (London)* 229:346 (1955)
12. Ellis, W.C., and Treuting, R.G., *Trans. AIME* 189:53 (1951)
13. Meussner, R.A., "Solidification of the Aluminum-Silicon Eutectic," NRL Report 5346 (to be published)
14. Rosenbaum, H.S., and Turnbull, D., "Metallographic Investigation of Precipitation of Silicon from Aluminum," General Electric Report No. 58-RL-2153, Dec. 1958
15. Weart, H.W., and Mack, D.J., *Trans. Met. Soc. AIME* 212:664 (1958)

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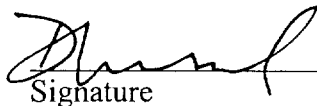
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-- SPEICAL ETCHANTS AND A CHEMICAL EXTRACTION TECHNIQUE. X-RAY
--
-- DIFFRACTION STUDIES HAVE BEEN USED TO CONFIRM THE METALLOGRAPHIC
-- OBSERVATIONS. ALTHOUGH THE DENDRITIC FORM OF THE PRIMARY A PHASE
-- WAS FOUND TO BE UNALTERED BY CHANGES IN THE GROWTH CONDITIONS, THE
-- FORM OF THE PRIMARY SI PHASE WAS NOT UNAFFECTED BY THESE CHANGES.
-- THE USUAL COMPLEX IDIOMORPHIC FORM OF THE SI PHASE WAS TRANSFORMED
-- TO THE DENDRITIC FORM WHEN GROWTH OCCURRED IN A SUPER-SATURATED
-- LIQUID. EUTECTIC SI PLATES, WHICH HAVE BEEN OBSERVED TO GROW FROM
-- PRIMARY SI PARTICLES, DOMINATE THE EUTECTIC TRANSFORMATION AND, BY
-- BRANCHING, RESTRICT THE GROWTH OF THE EUTECTIC A PHASE. THIS MODE
-- OF SOLIDIFICATION PRODUCES FINE EUTECTIC COLONIES IN THIS ABNORMAL
-- EUTECTIC STRUCTURE.
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