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SOLIDIFICATION OF THE ALUMINUM-SILICON EUTECTIC

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ABSTRACT

The eutectic solidification process in aluminum-silicon alloys has been examined through a metallographic study of slowly cooled and quenched specimens. The use of suitable etchants to delineate the structures of the Si and α phases and the examination of extracted particles of Si have shown that the abnormal Al-Si eutectic structure is the result of the great disparity in the nucleation and growth characteristics of the two phases. The eutectic Si not only nucleates readily, but it grows rapidly into a branched-plate structure. The nucleation of the α phase, requiring a high supersaturation, is retarded and, as a consequence, this phase exerts very little control in the solidification process. Thermal data, showing the relative effectiveness of the two primary phases in limiting the undercooling preceding the eutectic, support these observations.

PROBLEM STATUS

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

AUTHORIZATION

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INTRODUCTION

Portevin (1) classified eutectic structures according to form into four types, i.e., normal, abnormal, and two degenerate types. Recently Scheil and Zimmermann (2) have discussed eutectic crystallization using these same structural divisions. The aluminum-silicon eutectic structure has always been designated as abnormal, and in fact has become the most widely recognized and accepted example of all of the abnormal eutectic systems. The structural characteristics of this class of eutectics, as described by Scheil and Zimmermann, are defined by comparison with the normal eutectic. Although the abnormal eutectic may show some vestige of an orderly arrangement of the phases, the distinct pattern characteristic of the normal form is weak and often appears to be entirely absent. This abnormal form is attributed to the difference in the crystallization parameters (the nucleation and growth rates), of the two phases and, as a result of this difference, the interdependence or coupling of the crystallization processes of these phases is much weaker than in the normal eutectic. The kinetics of the growth of one of the phases dominates the eutectic transformation, and, as a consequence, no well-defined crystallization front exists during solidification. In the abnormal eutectic one phase is always present in much smaller quantity than the other. The eutectic particles of the minor phase usually take the form of plates or rods and are surrounded by mantles of the major phase. The observation, that isothermal eutectic arrests are obtained during the solidification of these alloys, indicates that the three-phase equilibrium of the eutectic is achieved and thus, that the envelopment of the minor phase by the mantle of the other eutectic phase is not complete.

From these characteristics of the abnormal eutectic it is clear that the two phases are not equals in determining the mode of solidification; one must dominate, or lead, the other. Scheil and Zimmermann (2) have stated that the minor phase becomes partially enveloped by the major phase. Since the Al-Si eutectic composition occurs at 12.7 w/o Si (3), this would imply that the Si phase leads and becomes partially covered with a mantle of a. (The a designation refers to the aluminum-rich terminal solid solution. The symbol Si is used here to designate the other terminal phase which is almost pure silicon.) Thall and Chalmers (4) in proposing a theory of modification envision the a phase as projecting beyond the Si at the eutectic:liquid interface during the solidification of the unmodified alloys. Most of the other investigators do not clearly define the growth conditions of the eutectic, but some, extrapolating from the observation of extensive a mantles around primary Si idiomorphs, seem to support the idea that the a phase dominates the transformation.

The evidence presented in all of these studies is based on thermal data and the examination of the structures of "unetched" metallographic specimens. Lacking suitable etchants the observations of these structures were limited to the shape, size, and distribution of the Si particles, the eutectic a phase appearing only as a structureless matrix. Thus, the limited metallographic evidence has not permitted a complete understanding of the solidification of these alloys, and no definitive study of this eutectic solidification process has appeared in the literature.

Some of the characteristics of the solidification process have been examined in preceding reports (3,5) on the redetermination of the Al-Si eutectic composition (12.7 w/o Si at 577.2°C) and the morphology of the phases of the alloys of this system. The reluctance of the primary a phase to nucleate and grow in the supersaturated liquid has been
demonstrated in the data for the hypoeutectic liquidus determination (3). In this work specimens which were held isothermally at temperatures 3° to 5°C below the liquidus for 30 to 60 minutes failed to reach equilibrium because of the sluggishness of the α nucleation. The nucleation of primary Si, on the other hand, was found to occur so rapidly that moderately fast quenching failed to suppress this precipitation completely. The details of the growth of the primary phases and their roles in the eutectic transformation, as revealed in the microstructures of a variety of alloy compositions, have been examined by means of special metallographic techniques. These observations (5) show that eutectic Si grows from the surfaces of primary Si, but eutectic α is not formed by the continued growth of primary α.

EUTECTIC UNDERCOOLING

From the metallographic evidence presented in these reports, it would appear that the presence of primary Si in the liquid sample should facilitate the initiation of the eutectic solidification. The observed undercooling preceding the eutectic in a series of alloys of varying silicon content shows that primary Si is very effective in initiating the eutectic. These data, plotted as a function of the cooling rate, are presented as Fig. 1. This figure includes the data from the small specimens used in a study of the phase diagram (3) and data obtained by the repeated remelting of somewhat larger samples of a 10.0 to 10.3 w/o Si alloy and those of a 12.8 to 13.0 w/o Si alloy.

Since the measurements of the undercooling were obtained by means of a centrally located thermocouple (Pt-Rh13), which can only sense the temperature at its hot junction, these measurements cannot be expected to define the true temperature at the site of the initiation of the eutectic transformation because in the general case this site must be assumed to be at some distance from the thermocouple bead. The disparity between the measured temperature and the actual temperature at the transforming site will naturally be greater the larger the specimen and the more rapid the cooling rate. Even under
standardized geometrical and thermal conditions, the observations will vary with changes in the distribution and population of eutectic sites within the specimen. As a consequence, scatter is to be expected in these data. This scatter is fully realized in the undercooling measurements shown in Fig. 1, but it is not great enough to mask the true effect of the primary phases in limiting the undercooling. The hypereutectic alloys, indicated by upright triangles in the figure, show very little undercooling even at rather rapid cooling rates. Hypoeutectic alloys, the open circle, show greater undercooling at comparable cooling rates. The eutectic alloy, the filled circle, shows much greater undercooling than any of the other alloys.

Only two data points from an alloy of eutectic composition are shown in the Eutectic field of Fig. 1. Most of the other points in this field, the inverted triangle, are from the repeated remelting of a number of specimens of a slightly hypereutectic alloy. The data from a sequence of remelts of one of these specimens, indicated by the small numbers adjacent to the data points, show a 3°C undercooling after the first remelting. After four remelts this had increased to more than 7°C. Similarly, the remelting of specimens of alloys containing 13.03 and 13.61 w/o Si increased the undercooling in these, thus moving the data points (upright triangles) from the Primary Si field to the Eutectic field. This change in the undercooling on remelting was not observed in the higher silicon alloys or in the hypoeutectic alloys. All the data points from the repeated remelting of the 10 w/o Si alloy specimen remained within the region designated as Primary α and no trend toward increasing or decreasing undercooling was evident in these data.

The foregoing observed change in undercooling of the slightly hypereutectic alloys was caused by segregation of Si through floatation of primary Si particles in the liquid alloy. The initial specimens, being quench-cast, were essentially free of large idiomorphic primary Si particles, and, as a result of the rapid solution of these, very little segregation was produced on melting for the first measurements of the undercooling. During the slow cooling of this first experiment large idiomorphs of Si were formed, but since these alloys were of high purity, almost all of these were grown and anchored at the specimen surfaces. On remelting some of these surface Si particles became detached through partial solution and floated to the top of the specimen. Through the floatation of primary Si during remelting, a nonhomogeneous liquid was produced, and when the process was repeated many times, the liquid in the lower section of the specimen approached the eutectic composition. Thus, the observed undercooling in these alloys tended to increase with repeated remelting and move from the Primary Si field to the Eutectic field (Fig. 1). In the high silicon alloys, this effect is not evident after one or two remelts because the required segregation had not been achieved. In more impure alloys where much heterogeneous nucleation of the primary Si phase occurs in the body of the liquid, this effect would be much more pronounced than in these alloys where the specimen surface affords the only effective sites for heterogeneous nucleation.

EUTECTIC SOLIDIFICATION

The Role of Primary Si

The above interpretation of the undercooling data of Fig. 1 is substantiated by microstructural observations. As shown in Fig. 2, eutectic Si plates are frequently observed to grow from the surface of primary Si particles. The orientations of some of the plates, which are not connected to the primary particle in this plane of polish, suggest that these also originated at the primary surface even though not all of the primary Si particles show this high population of eutectic growth in each plane of polish.

The primary Si particles chemically extracted from the alloys failed to show extensive development of eutectic plates, but this observation may merely attest to the fragility of these thin eutectic plates which may have been broken from the primary surface during
Fig. 2 - Eutectic Si plates grown from the surface of a primary Si idiomorph, etched with modified CP-4, 240X

extraction, washing, or handling. Figure 3 shows the complex surface structure of an extracted primary Si particle. White areas in the foreground of the sketch* are sections of the particle exposed in a metallographic plane of polish before the particle was extracted from the alloy. The lines in these areas were delineated by the CP-4 etch applied to the metallographic specimen. A number of small projecting plates are seen on the growth surfaces of this primary Si idiomorph. These may be the stumps from which the eutectic plates grew. The population of these projections on the surfaces of idiomorphic Si particles is so low that the probability of observing more than a few of these in any section of the structure is very small. The orientation dependence of Si plates adjacent to a primary Si particle is much more readily detected in the microstructures because these plates, narrow at the junction with the primary particle, are broad and long.

Since eutectic Si has been shown to grow and take its orientation from primary Si particles, the undercooling required for the initiation of the eutectic in hypoeutectic alloys is small. With increasing silicon content, the observed undercooling decreases because the number of sites, and thus, the probability of initiating the eutectic structure increases.

*Because of the limited depth of focus of the metallograph, it was necessary to sketch the particle of Fig. 3a in order to show the details of the various faces.
plates do grow from the primary particles of this phase (Fig. 2). Anodized specimens have revealed a distinct boundary between the primary and eutectic α phases (Fig. 4) indicating that the eutectic grains are not formed by the continued growth of the primary α. The examination of these etched microstructures has also shown that the Si plates usually span the α grains of the eutectic and not infrequently pass through more than one of these grains. A photograph of the top surface of a specimen of a 13 w/o Si alloy (Fig. 5) illustrates more clearly than the random section afforded by metallography the growth of eutectic Si from a primary particle, the dendritic or branched form of the eutectic plate structure, and the continuity in this network of fine Si plates. From these observations, it seems reasonable to conclude that the Si phase dominates in determining the eutectic structure. It not only nucleates easily, but it grows rapidly and projects ahead of the eutectic α phase into the liquid. The α phase, requiring greater supersaturation for nucleation, forms on the sides of the eutectic Si plates and grows along these plates. Under normal solidification conditions it does not overtake the growing edge of the Si plate. The fine grain size of the eutectic α results from the branched growth of the Si plates. These plates effectively restrict the growth of the eutectic α grains so that the continuation of the eutectic solidification requires the renucleation of the α phase among the Si branches. Since there is very little evidence of any preferred orientation relationship between the Si and the α phases, the eutectic α grains show random orientations.

Fig. 5 - Top surface of a 13 w/o Si alloy specimen showing primary and eutectic Si, 400X

QUENCHED STRUCTURES

Photomicrographs of selected areas of a specimen of a 13 w/o Si alloy are presented in Figs. 6, 7, and 8. This alloy was slowly cooled to the eutectic, allowed partially to solidify isothermally, and then quenched. The origin of the structures found in this sample can be adequately explained in terms of the proposed mechanism of solidification. Since a large number of events are depicted in each of the photomicrographs and since the perspective provided by the plane of polish is biased, not all of the aspects of the transformation are equally well represented. These figures do, however, present a reasonable view of the variety of structures observed in the large number of samples examined in this research.
Fig. 6 - A section of a 15 w/o Si alloy specimen quenched after partial solidification at the eutectic temperature, anodized, bright field illumination, 40X.

Fig. 7 - Long Si plates formed at the eutectic liquid interface during the quench, same specimen as Fig. 6, 80X.
The eutectic structure formed isothermally around the idiomorphic Si particle of Fig. 6 is typical of the abnormal eutectic. There is no extensive mantle of \( \gamma \) about the primary particle; and, even in the recesses of this Si particle, there is no divorce of the eutectic phases. Because of the complex form of this particle, the orientation dependence of the eutectic Si about the primary particle is not easily recognized in this photomicrograph. However, the continuity of some of these plates with the primary particle is clear. Beyond the usual eutectic structure a zone is found which contains long plates of Si. These plates are prominent because they are delineated by mantles of \( \alpha \) in a background of fine eutectic structures. This zone marks the location of the interface between the eutectic structure and the liquid at the time of quenching. As the rate of heat extraction increased, the eutectic Si plates projecting ahead of their \( \alpha \) mantles at the existing interface grew rapidly into the supercooled liquid and produced these long plates. Since a large temperature gradient was quickly established along these plates, the probability of eutectic \( \gamma \) nucleating on these surfaces was high and \( \alpha \) mantles developed rapidly enough to stifle, almost completely, the natural branching of this eutectic Si. The structure of Fig. 7, showing the area between two impinging growth centers, contains a number of these long Si plates and illustrates the deep penetration of these into the liquid.

The growth of these long Si plates was terminated when the rate of heat extraction became large enough to permit the growth of the \( \alpha \) mantles to overtake the Si plates. The mantles enveloped the Si plates, and the eutectic solidification beyond this stage required the renucleation of the Si phase; growth of these mantles provided the required regions of low silicon concentration to assist this renucleation. The structure which emanates from these sites has the appearance of a normal lamellar eutectic. Thus the conditions at these sites must be such that the nucleation and growth rates of the \( \alpha \) and Si phases are nearly equal. In this manner, all of the liquid which was left behind the ill-defined solidification front was finally frozen as a fine, almost lamellar, structure. Beyond the zone containing the long Si plates in Fig. 6, the eutectic becomes increasingly fine, and finally, \( \alpha \) dendrites
appear as the primary phase in the structure. The formation of fine α dendrites indicates that the liquid in this region had undercooled to such a low temperature that the probability of α nucleation exceeded that for Si. As might be expected the rate of nucleation of α was not large. The dendrites, thin because the accumulation of silicon in the liquid during growth initiated the eutectic, are very long. Usually these α dendrites can be traced back to the surface of the specimen. Those shown in Fig. 6 appear to have originated at the surface of the specimen in a region which was free of solids at the time of the quench. The area shown in this figure includes the zone of impingement of this structure and that originating from the isothermal eutectic structure.

At one site near the bottom of this same specimen a number of primary Si particles were observed which were probably largely surrounded by liquid at the time of the quench. The structure which formed in this region is shown in Fig. 8. As a result of the rapid drop in temperature at this surface site during the quench, the development of the usual eutectic structure was suppressed. Eutectic Si was nucleated only at a few preferred sites on the surfaces of the primary Si particles before the undercooling became great enough to allow the nucleation of the eutectic α phase in the silicon-lean liquid at these surfaces. Though not complete, the envelopment of the primary Si by α is extensive. A fine eutectic structure formed in the few areas where eutectic Si particles penetrated the depleted layer before envelopment by α. The formation of an extensive α mantle about primary Si occurs only when great undercooling is achieved by rapid cooling; it is not a part of the normal eutectic solidification process.

On the rather smooth surfaces of the idiomorphic Si particles, extracted from slowly cooled hypereutectic alloys, fine networks of lines were always observed. This cellular pattern is shown in the photograph of Fig. 3 and has been accentuated in the sketch (Fig. 3a). Since the size and shape of the cells of this pattern match those of the eutectic α grains in slowly cooled specimens, this network of lines is viewed as an imprint of the eutectic α grains on the idiomorphic Si surface. This network, however, shows very little correspondence to the other growth features of the primary Si surface. As a result, it is proposed that the eutectic α grains which produced these markings were not nucleated on this surface, but rather that these grains were nucleated on the eutectic Si plates which grew from or around this surface. These grains then grew to impinge upon and impress their outlines on the surface of the primary Si particle.

The surfaces of Si idiomorphs which became enveloped by α during rapid cooling did not show this cellular structure; the only growth pattern visible on these surfaces were very fine striations and dendritic ridges. Striations and ridges similar to these were shown underlaying the cellular pattern on the slowly cooled Si particle of Fig. 3b. An examination of acidified metallographic specimens containing α-enveloped primary Si (Fig. 8) revealed that the α mantles were very coarse grained. In most cases only two or three α grains were detected in the entire sheath surrounding each Si particle in these sections. Thus, in forming the α envelope, nucleation must only occur at a very few sites on the primary Si surface. The α grains growing from these surface sites spread along the surface of the idiomorph and, as a result, no cellular grain boundary pattern is impressed on these surfaces.

**SUMMARY**

The formation of the abnormal eutectic structure in Al-Si alloys is the result of the disparity in the nucleation and growth characteristics of the constituent phases. The eutectic Si phase not only nucleates readily, but it grows rapidly into a branched-plate structure. The nucleation of the α phase, requiring a rather high supersaturation of the liquid, is retarded and, as a result, this phase exerts very little control in the solidification process. Since the eutectic Si phase projects ahead of the eutectic solid into the liquid, the eutectic α phase is relegated to the role of forming the matrix around the existing Si plates.
The eutectic α grains are nucleated on the surfaces of the Si plates and grow along them. At slow growth rates, the α grains seldom overtake the leading edges of these plates. With increased cooling rates, the disparity between the growth kinetics of the two phases is reduced, and with sufficiently rapid cooling, they may become nearly equal. When this latter condition is achieved, the branching of the eutectic Si is effectively suppressed by the growth of the eutectic α and a rather normal lamellar structure is formed.

In the slowly cooled alloys, the branching of the eutectic Si phase effectively restricts the growth of the eutectic α phase. Since the continued growth of the eutectic α requires the renucleation of the α phase beyond the obstructing Si plate and since no preferred orientation relationship between the α and Si appears to exist, the eutectic α grains of the matrix are small and randomly oriented.

The role of the primary phases in initiating the eutectic structure has been examined by thermal analysis and by metallography. These observations indicate that eutectic Si does grow from the surfaces of primary Si particles, and thus, these particles are very effective in initiating the eutectic solidification. Eutectic α does not grow from the surfaces of the primary α dendrites. The presence of primary α in the alloy assists the formation of the eutectic only indirectly through the creation of a liquid layer supersaturated with silicon adjacent to the growing α dendrites.

The development of extensive α mantles around primary Si particles has been found to occur only when great undercooling is achieved by rapid cooling. They are not present in the structures of slowly cooled alloys.

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REFERENCES

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