

論 文

# An Assessment of the Role of Rare Earth in the Eutetic Modification of Cast Aluminum-Silicon Alloys

B. J. Ye\*

알루미늄 - 실리콘 합금주물의 공정조직 개량처리에  
미치는 희토류 금속의 역할에 관한 평가

예 병 준\*

## 초 록

I A쪽과 II A쪽이 Al-Si 합금의 공정조직개량 처리에 효과적인 것은 잘 알려진 사실이나 Na(Sodium)과 Sr(Strontium)만 상업적으로 쓰여지고 있다. 그러나 휘발성과 산화하기 쉬운점때문에 Na은 그 양을 정확하게 조절하기가 어렵고 특히 온도가 높은 경우 더욱 곤란하나 Sr은 휘발성이나 산화성은 없으나 micro-또한 macro-porosity의 주 원인으로 보고 되고 있다.

희토류 금속(예: Cerium, Lanthanum, etc)도 개량처리 효과가 있다는 논문들(ref. 2, 3, 4, 5)이 있고, 계속 연구되어 오고 있으나 그 세부사항과 효율성에 관해 정립된 바가 없다. 이런 연유로 Al-Si 합금의 생산을 위한 개량 처리제로서의 희토류 금속의 역할에 대해 구체적이고 세부적인 개량처리기구의 구명을 위해 이 연구가 이루어졌다. Al-Si 합금 356가 채택된 이유는 상업적 Al 주물의 생산을 감안해서 였다.

## 1. INTRODUCTION

It is well recognized that the Group IA and IIA elements are effective modifiers of the aluminum-silicon eutectic, however, only sodium and strontium have been used extensively in commercial production of these alloys (1). Because of the volatilization and oxidation losses which occur it is often difficult to accurately control the results of sodium modification. Foundrymen find it particularly difficult to retain the effect of sodium where extended holding times are encountered (fading) or where higher temperatures are required. In addition, the amount of sodium carried through in remelting is subject to considerable change as the processing conditions are altered. Strontium is

an effective modifier of the aluminum-silicon eutectic, and is not subject to the volatilization and oxidation effects characteristic of sodium, but its use reportedly results in an increase in the micro-and macro-porosity in the cast aluminum-silicon alloy.

The literature reports that rare earth elements (e.g., cerium, lanthanum, etc.) are capable of also modifying the eutectic structure of cast aluminum-silicon alloys (2, 3, 4, 5). While the role of mischmetal as a eutectic modifier and as a beneficial alloy addition has been studied, the details of using this technique and the effectiveness of this treatment has not been set forth (3).

Rare earths (added as mischmetal) are reported to modify the structure of both sand and chill cast aluminum-silicon alloys, but an addition of about 1% rare earth is required. The tensile strength of an Al-13%

\* 1985년도 학술대회에 발표된것임. (1985.11.9)

\* 현대자동차주식회사 마북리연구소

Si alloy produced with a 1% rare earth addition was reported to be 2.3-2.9 kg/sq.mm. higher than that obtained from a sodium modified version of the same alloy (7). The elongation and hardness were also reported to increase with this rare earth treatment. Later work reports the high temperature properties of these alloys and provides somewhat more detail (5). A 67% increase in the tensile strength at 392°F (200°C) was reported with rare earth treatment, although no change in strength was observed at 752°F (400°C). The elongation, however, increased 39% at 392°F (200°C) and 44% at 752°F (400°C).

Rare earths have been added to these aluminum-silicon alloys as mischmetal, but also in the form of specific rare earth metals and as rare earth fluorides. It was reported that cerium, lanthanum and neodymium partially modified the eutectic structure (2, 3, 4, 5, 6). Where rare earth fluorides were used, a refinement of both the polyhedral silicon plates and the eutectic was reported, however, complete modification of the structure was never achieved in sand castings. Other research has reported that yttrium is also capable of modification of the eutectic structure, but no details concerning this technique have not been made available (6, 7, 8).

In his study of this procedure, Sharan (3, 4) reported that the modification reported with rare earths can be explained using the critical growth temperature hypothesis of Kim (9), i.e., the modifying element should have a tendency to form compounds with the precipitating phase (silicon) at a temperature below the normal eutectic temperature, but that this modifying element should exhibit little compound forming tendency with (and have low solubility in) the solvent phase (alpha aluminum). Lanthanum meets most of these requirements, but cerium and neodymium satisfy them only partially. These rare earth were reported to form a variety of compounds with aluminum and silicon (e.g.,  $Al_4Ce$ ,  $Al_2Ce$ ,  $SiCe$ ,  $SiCe_2$ ,  $SiCe_4$ , etc.). Nucleation is suppressed to the temperature of globular growth thus modifying the structure. The lack of complete modification in sand castings is left unexplained.

The reported increase in tensile strength has been attributed to the modification of the eutectic structure, and to the strengthening effect of a fine dispersion of intermetallic compounds (6, 20, 23). However, little

supporting evidence has been presented in support of this concept (e.g., eutectic undercooling, secondary dendrite arm spacing, hardness, etc.).

As a result of the lack of details available and the questionable reliability of the inferred procedures presented in the literature concerning the potential of using rare earths as a modifying agent in the production of cast aluminum-silicon alloys, this study was conducted to obtain further insight as to the operable modification mechanism. In order to relate to commercial aluminum casting production, the study was conducted using a standard hypoeutectic aluminum-silicon alloy, 356.

## 2. PROCEDURE

### 2.1 Casting Production

Commercial 356 alloy ingot (7.3% Si, 0.34% Mg, 0.25% Fe, 0.04% Ti) was melted in an alumina crucible in a resistance furnace, heated to 1350F (732C) and degassed with hexachloroethane tablets. An adjustment for magnesium loss was then made, and the modification agent plunged into the melt using a graphite rod. Sodium modification was made using high purity sodium (canned), while rare earth modification was made using mischmetal (60% Ce, 24% La, 10% Nd, 6% Pr). The first treated sample was cast within a minute after modification, and subsequent samples (20, 60 and 120 min.) were cast at  $\pm 10F$  (6C). Both sand and graphite molds were used.

### 2.2 Thermal Analysis

Solidification cooling curves were obtained from both untreated and treated melts cast into both and [0.75 in. (19mm) and 1.5 in (38mm) D.] and graphite molds [1.25 in. (32mm) D.]. A chromel-alumel thermocouple was placed near the center of the casting to record the cooling curve and to determine the eutectic arrest and undercooling temperatures.

### 2.3 Metallographic Analysis

Metallographic samples were obtained from the castings adjacent to the thermocouple bead and prepared for study using conventional optical microscopy, scanning electron microscopy and transmission electron microscopy. The SEM analysis was conducted on deep

etched samples prepared using an etchant of 5% HCl plus 2% HF. These studies were used to observe the silicon phase morphology. TEM samples were ion thinned from 0.002 mm. and were used to establish the growth direction of the silicon particles. Normal metallographic techniques were used to determine the secondary dendrite arm spacing at four or five locations (the average value reported in the data).

### 3. RESULTS

The effect of mischmetal treatment on the undercooling obtained in the 356 alloys is presented in Figures 1 and 2. The effect of holding time for a 2% mischmetal

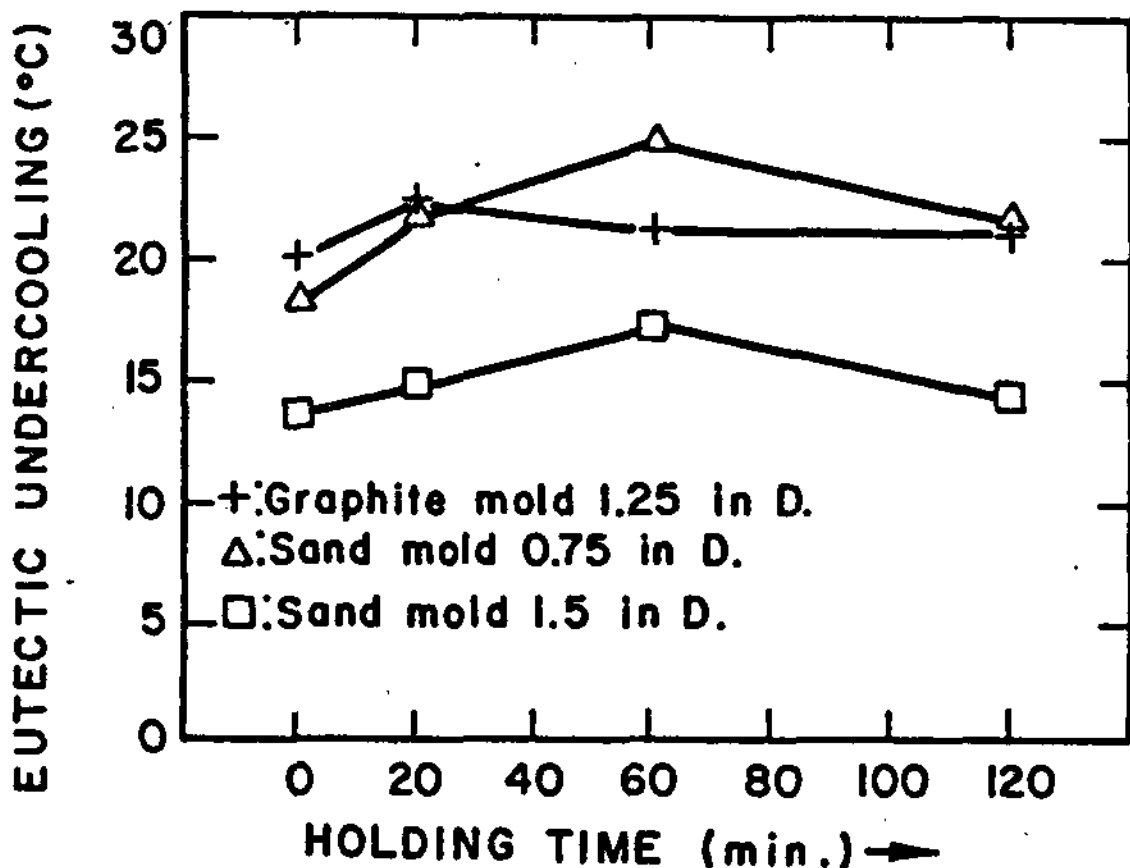


Fig. 1. Fading effect of 2.0% misch metal modified 356 aluminum alloy as indicated by eutectic undercooling.

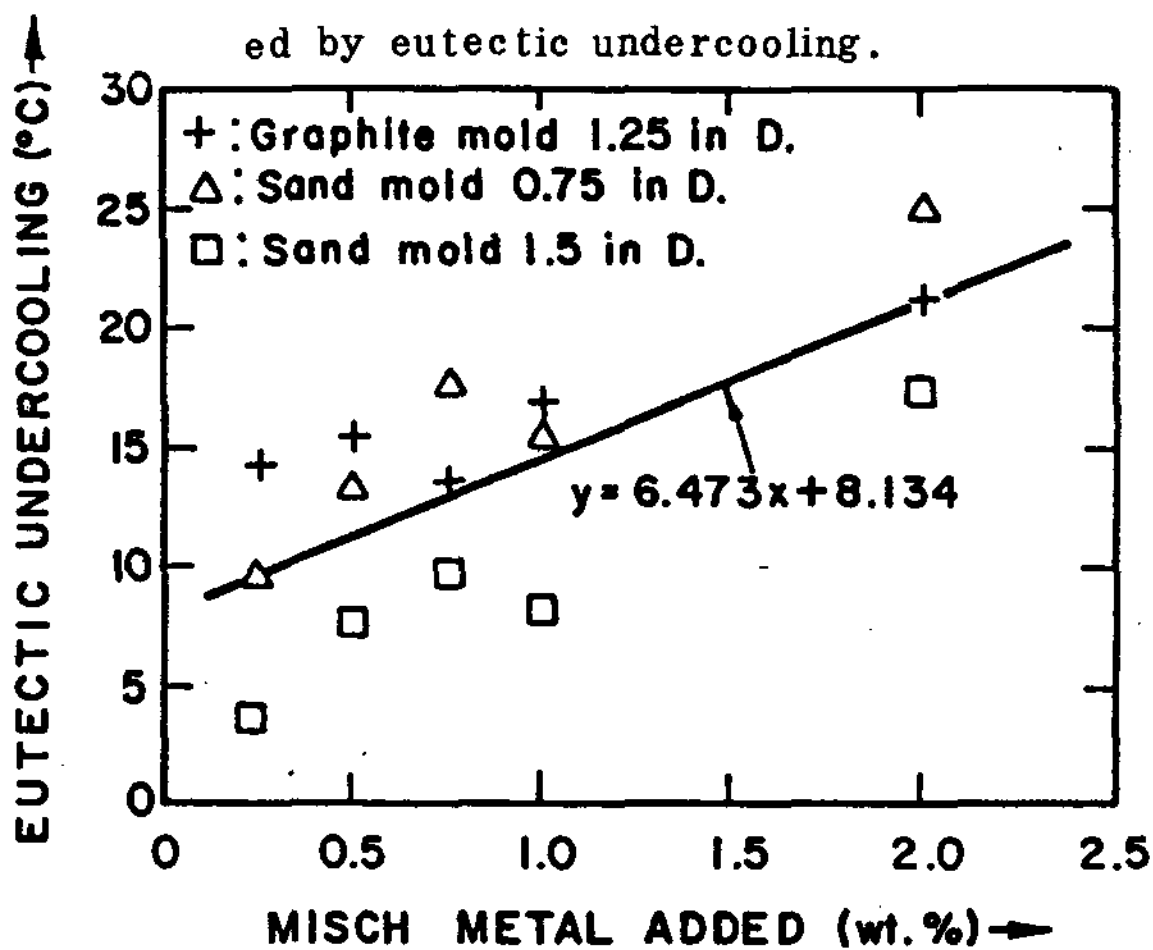


Fig. 2a. Influence of the amount of misch metal added on the amount of eutectic undercooling.

undercooling. The curve shown (and regression equation) is based on all of the data shown.

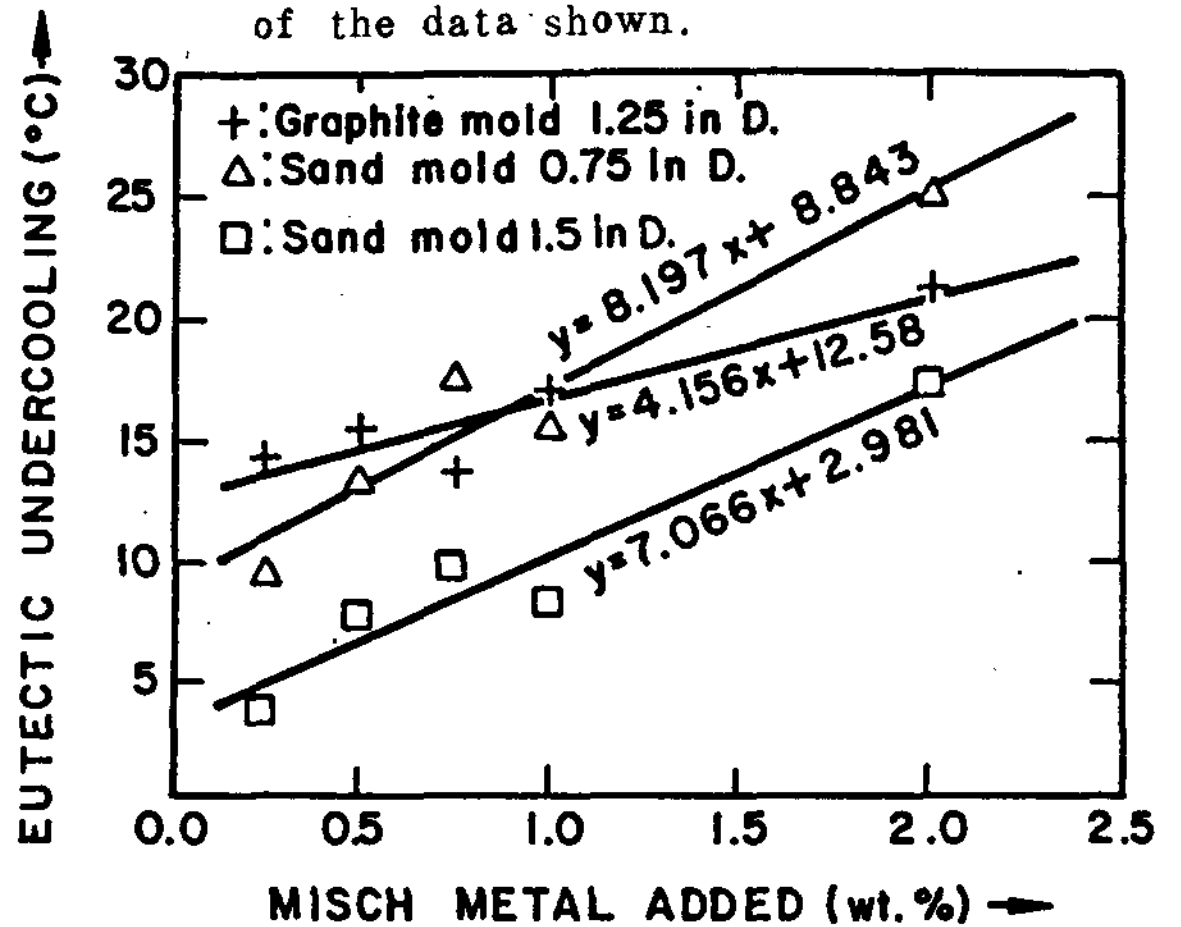


Fig. 2b. Same as Fig. 1a, except that data for each casting has been evaluated separately. Note that the slope of the curve for the graphite mold (rapid cooling) is different than that for the sand molds.

treatment is demonstrated in Figure 1, where it may be observed that the undercooling continues to increase up to 60 minutes after treatment, but that even up to 120 minutes after treatment there is little change undercooling. In sharp contrast, treatment with 0.035% Na beings to fade after only 10 minutes and the effect in a san cast mold is rapidly lost, Figure 3. The effects of rare earth treatment increase linearly as the amount of rare earths are increased, up to 2% mischmetal, Figure 2.

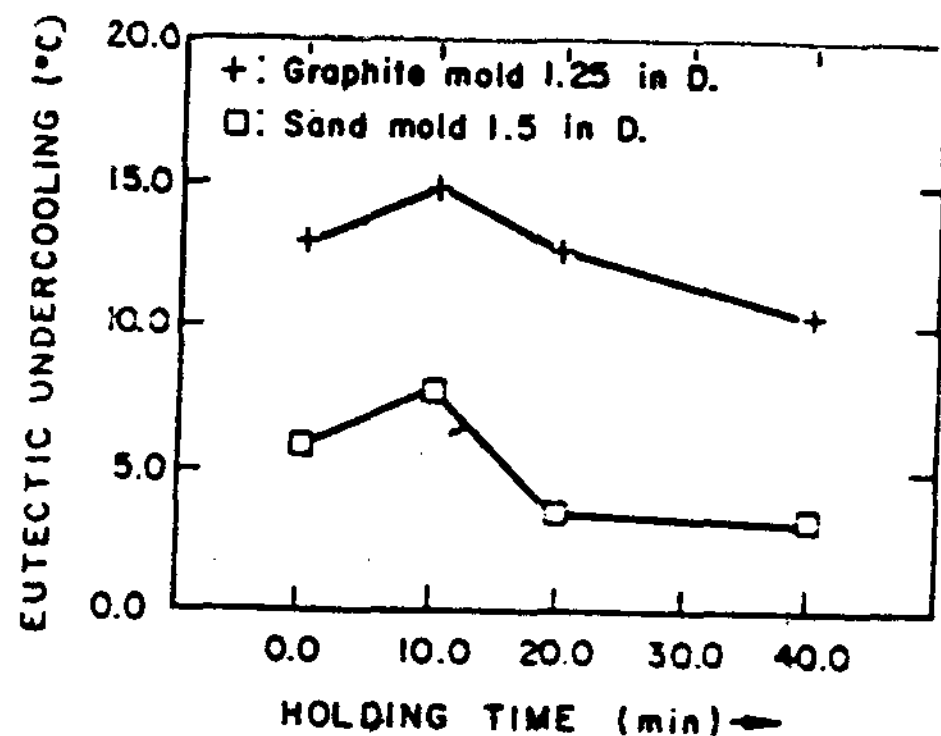


Fig. 3. Fading effect of Sodium modified 356 aluminum alloy as indicated by eutectic undercooling.

Microstructural changes encountered in the use of rare earths as a eutectic modifier are depicted in Figures 4, 5 and 6. This series of photomicrographs illustrates

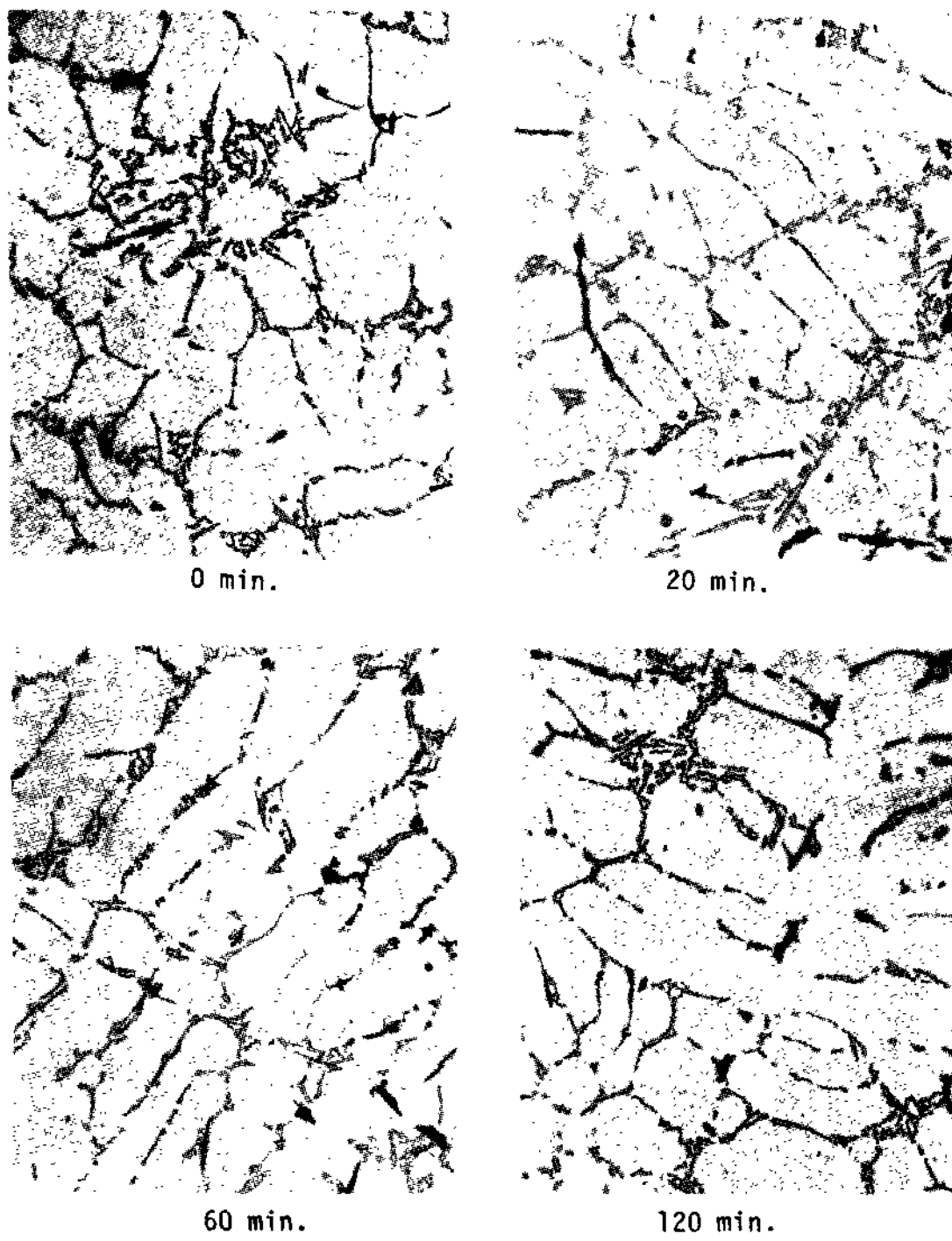
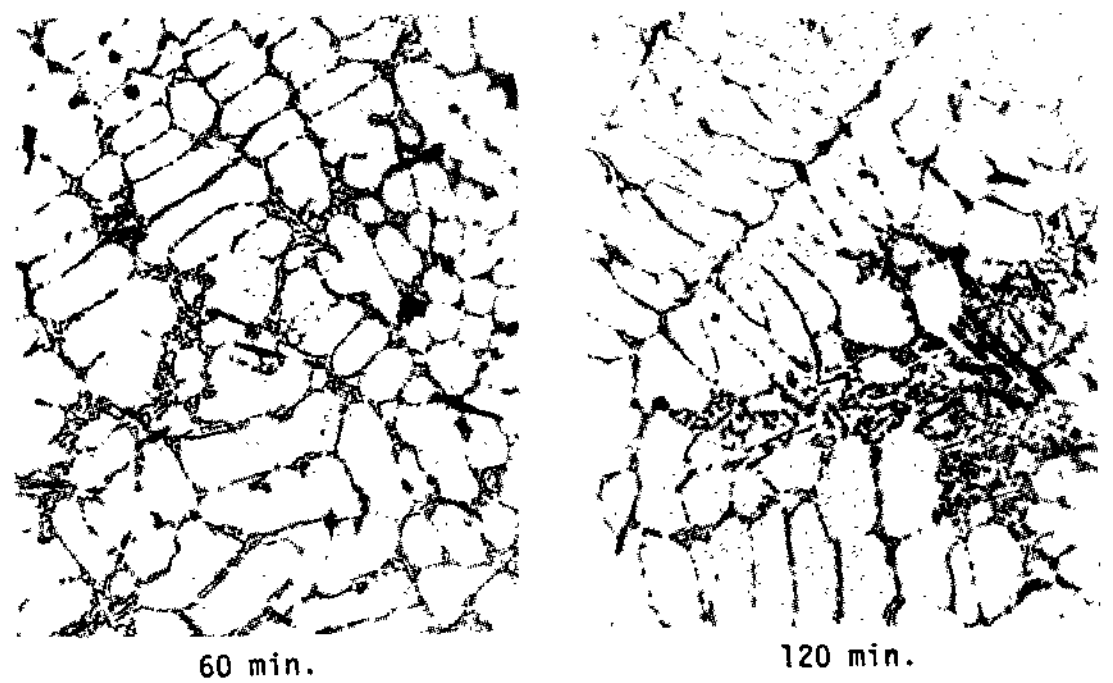
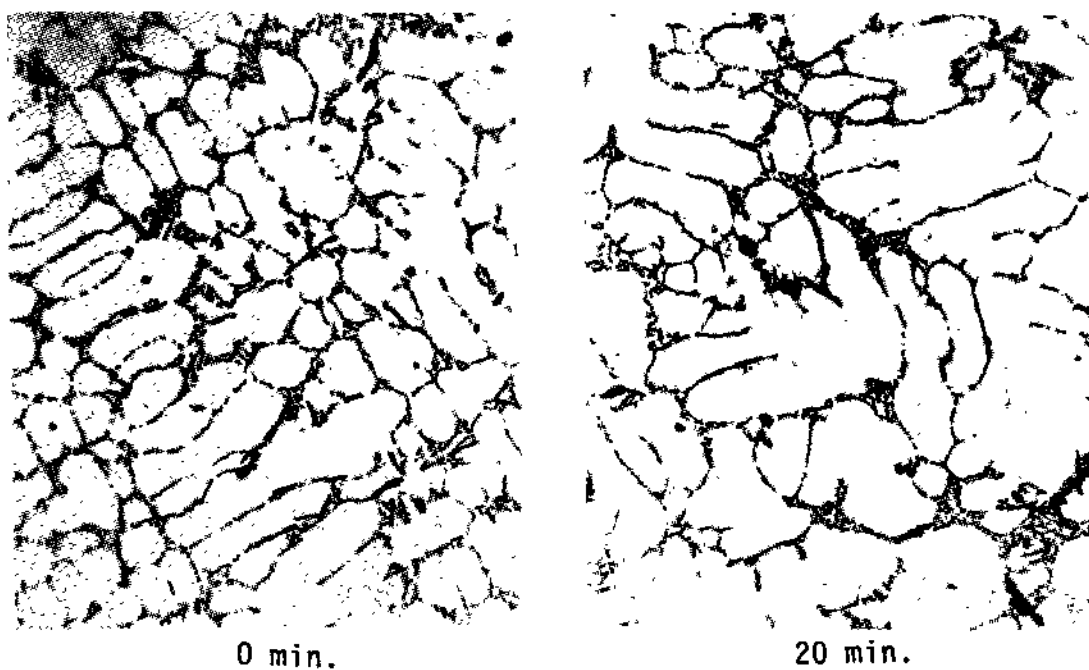
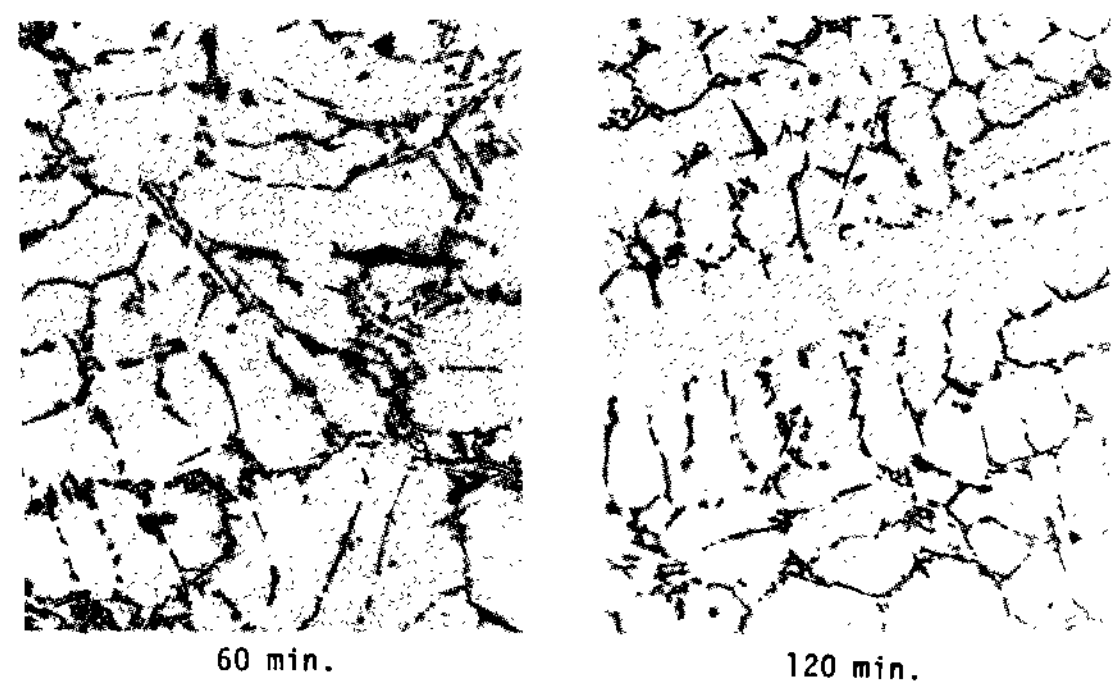
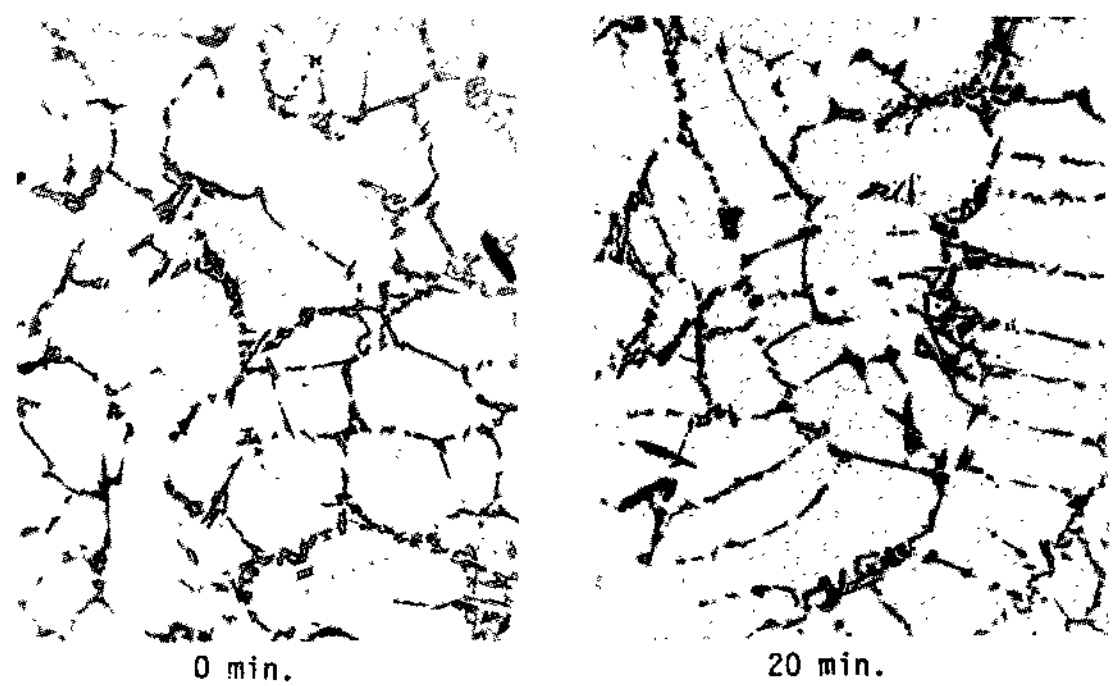


Fig. 4. Effect of holding time on the microstructure of the 0.75 % misch metal modified 356 aluminum alloy cast into a 0.75 in.D. Sand mold. Etched, 0.5 % HF, 200X.



a ) 1.25 in.D. graphite mold.

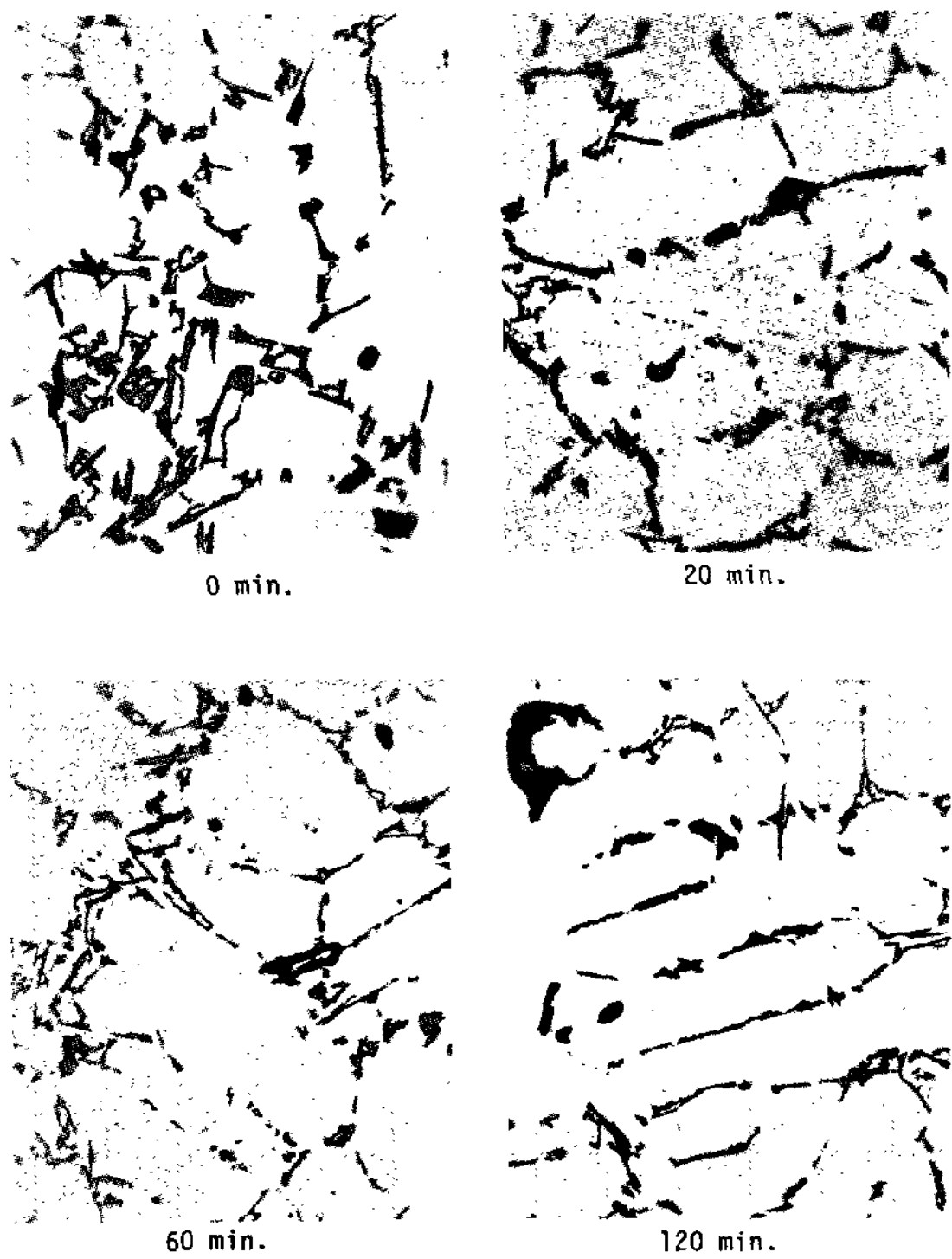
Fig. 5. Effect of holding time on the microstructure of the 1.0 % misch metal modified 356 aluminum alloy.



b ) 0.75 in.D. sand mold.

Fig. 5. Continued.





c) 1.5 in.D. sand mold.

Fig. 5. Continued.

the effect of the amount of rare earths added (0.75, 1 and 2 percent), the effect of holding time (up to 120 minutes) and the effect of solidification cooling rate (1.5 and 0.75 in D. and molds, and a 1.25 in. D. graphite mold). The following observations can be made:

- a. At 0.75% rare earth treatment no eutectic modification was obtained in the sand molds, and only partial modification was attained in a graphite mold.
- b. Some eutectic structure modification could be seen in the 0.75 in. D. sand cast section with a 1% rare earth treatment, but no modification was found in the larger sand cast section.
- c. With a 2% rare earth treatment, complete modifica-

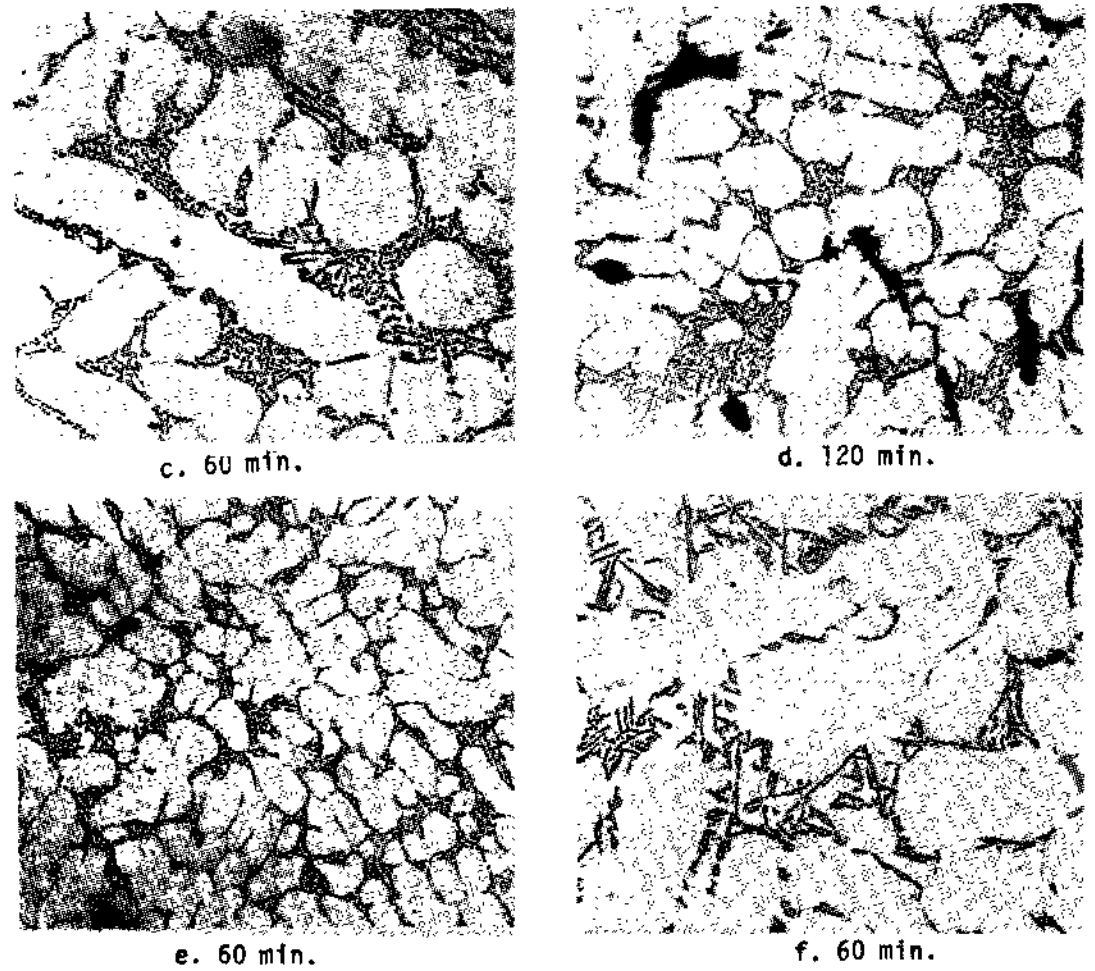
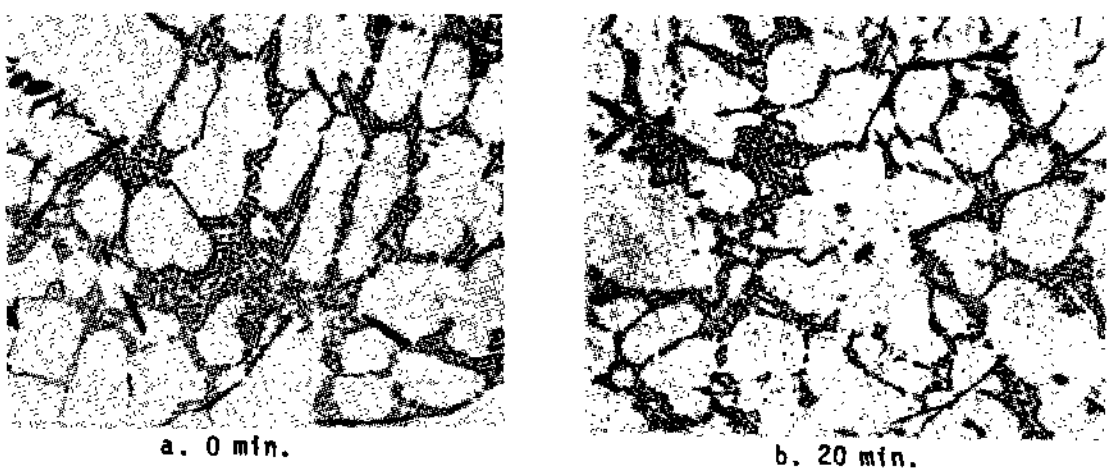


Fig. 6. Effect of holding time on the microstructure of the 2.0% misch metal modified 356 aluminum alloy. a through d) 0.175 in.D. sand mold. e) 1.25 in.D. graphite mold. f) 1.5 in.D. sand mold. Etched, 0.5% HF, 200X.

tion was obtained in the graphite mold, and substantial modification of the eutectic structure attained in the 0.75 in. D. sand mold.

The effect of rare earth, sodium and strontium treatment on the secondary dendrite arm spacing for

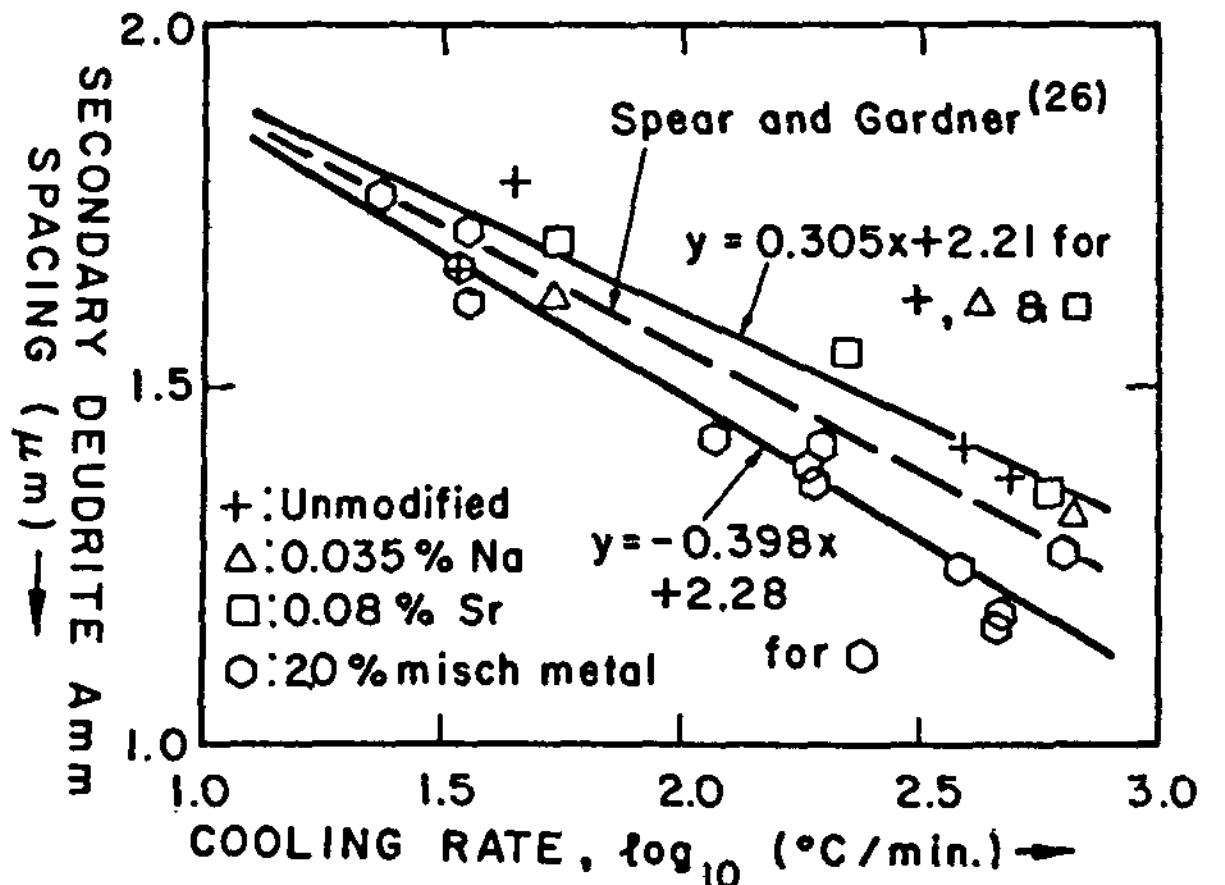


Fig. 7. Effect of solidification cooling rate on the secondary dendrite arm spacing of 356 aluminum alloy.

different castings is presented in Figure 7. No difference was observed in the secondary arm spacing for sodium and strontium treated melts, however, a 2% mischmetal

treatment results in a definite reduction in the secondary dendrite arm spacing.

Changes in the silicon phase morphology with rare earth and sodium treatment are evident in the scanning electron microscope photographs presented in Figures 8 and 9. While the silicon plates usually appear in a

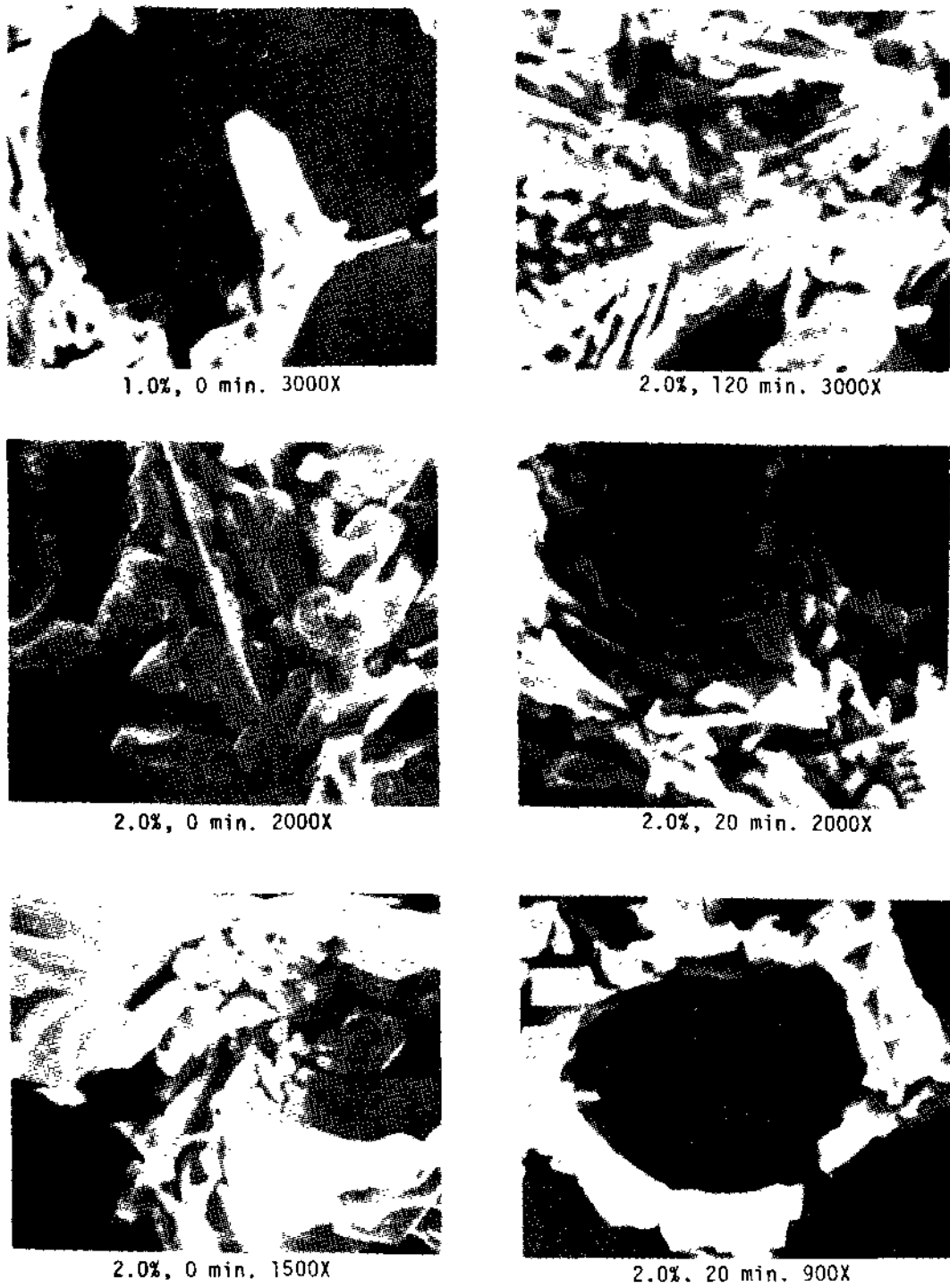


Fig. 8. Silicon phase morphology of misch metal modified 356 aluminum alloy. a) 1.25 in.D. graphite mold. b) 0.75 in.D. sand mold. c) 1.5 in.D. sand mold. SEM photographs, Etched, solution of 1.0% HCl and .5% HF.

somewhat lammelar form in the untreated alloys, treatment with rare earths or sodium alter the shape of the silicon phase. For example, rare earth treatment

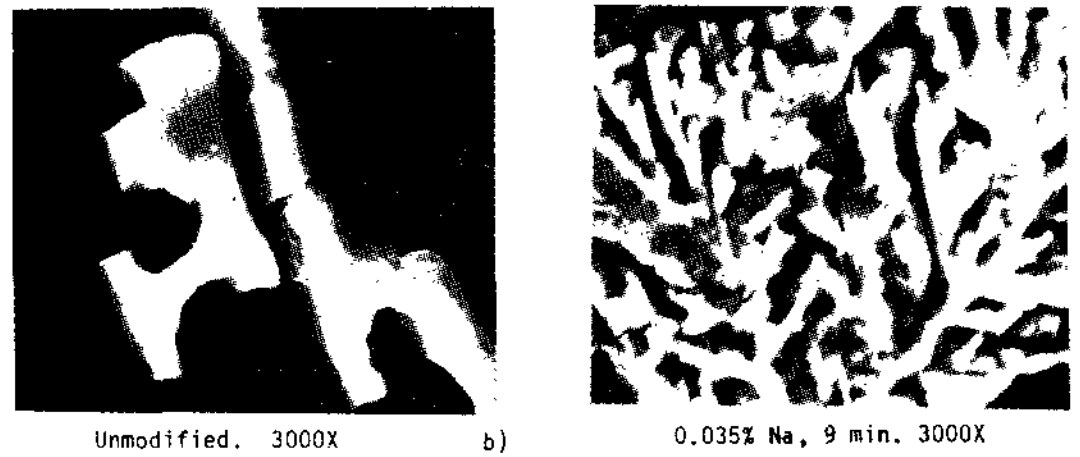
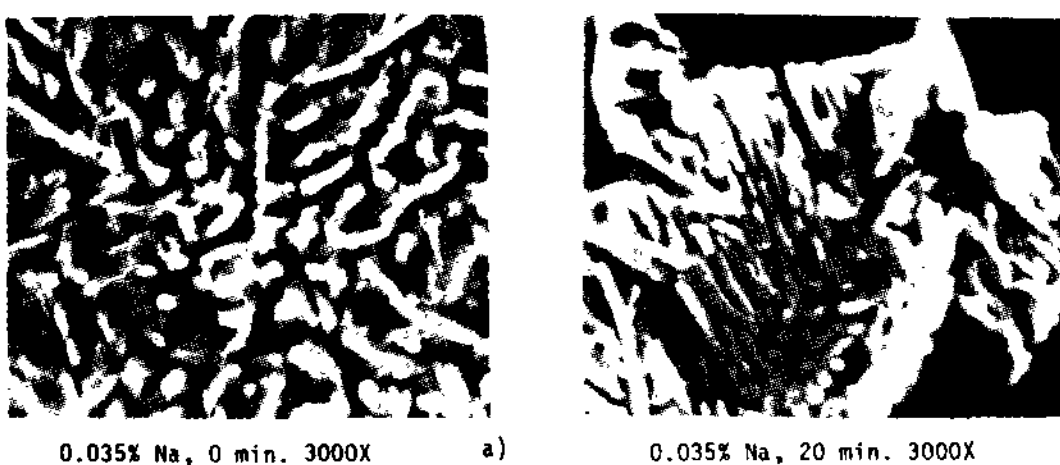


Fig. 9. Silicon phase morphology of sodium modified 356 aluminum alloy. a) 1.25 in.D. graphite mold. b) 1.5 in.D. sand mold. SEM photographs. Etched, solution of 1.0% HCl and .5% HF.

changes the silicon phase to a rosette or semideveloped, branched fibrous form depending upon the casting solidification cooling rate. The changes in silicon

Table 1. Summary of Silicon Phase Morphology Attained in Different Castings

	Graphite Mold	Sand Mold, 0.75 inch	Sand Mold, 1.5 inch
Unmodified	Plate, sometimes lamellar		
1% MM Added	Interconnected rosette		
2% MM Added	Interconnected filamentary fibrous less rosette	Interconnected filamentary rosette and branched fibrous	Interconnected rosette
.035% Na Added	Interconnected filamentary, branched rod, coral		Interconnected coral, chain-like

morphoogy are summarized in Table I.

The relationship of treatment and casting solidification cooling rate on the hardness (HB) is shown in Figure 10. The values obtained for sodium and strontium treatment fall within the data band for rare earth treatment. The untreated castings exhibit a somewhat higher hardness. Little effect was observed in the influence of sodium or rare earths on the microhardness of the alpha aluminum, Tables 2 and 3.

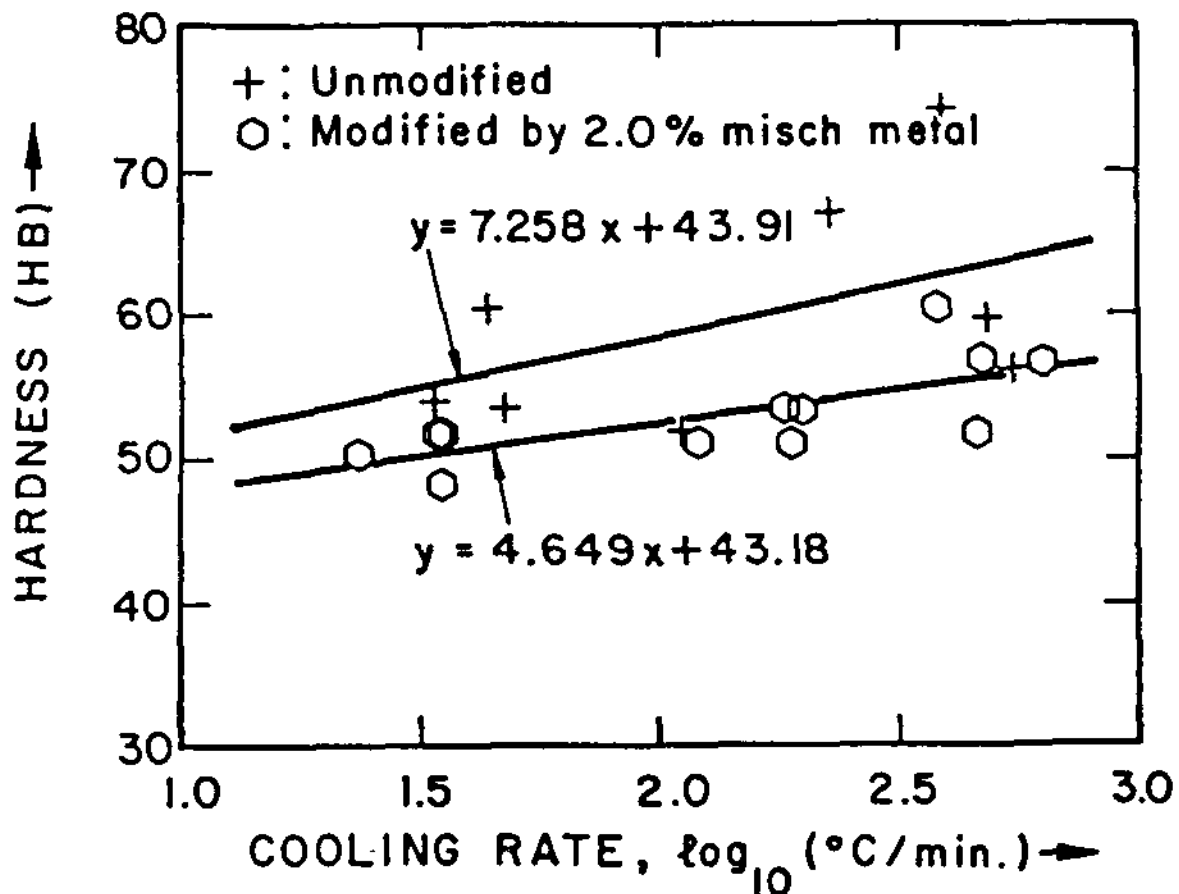


Fig. 10. Effect of solidification cooling rate on the Brinell hardness of 356 aluminum alloy.

Table 2. Microhardness (Hv) Obtained in 2.0% Misch Metal Measurements Obtained within the Primary Alpha Phase 10 g. Load Indentor

Holding Time/Mold	Graphite Mold	Sand Mold 3/4 Inch	Sand Mold 1 1/2 Inch
0 Minutes	56.59	54.88	57.42
20 Minutes	51.45	47.00	50.76
60 Minutes	48.74	59.12	45.09
120 Minutes	46.53	46.82	47.07

Table 3. Microhardness (Hv) Obtained in 0.035% Na Modified 356 Aluminum Alloys Measurements Obtained within the Primary Alpha Phase 10 g. load indentor

Holding Time/Mold	Graphite Mold	Sand Mold 3/4 inch	Sand Mold 1 1/2 inch
0 minutes	47.45	58.14	51.63
10 minutes	62.11	56.84	49.04
20 minutes	46.50	51.92	48.85
50 minutes	45.81	55.75	52.03

The distribution of rare earths in the microstructure of the aluminum-silicon alloys was found to be related to the silicon phase as is evident in the element distribution maps presented in Figures 11 and 12. This is further demonstrated in the data of Tables 4 and 5 and in Figure 13. A summary of these results follows:

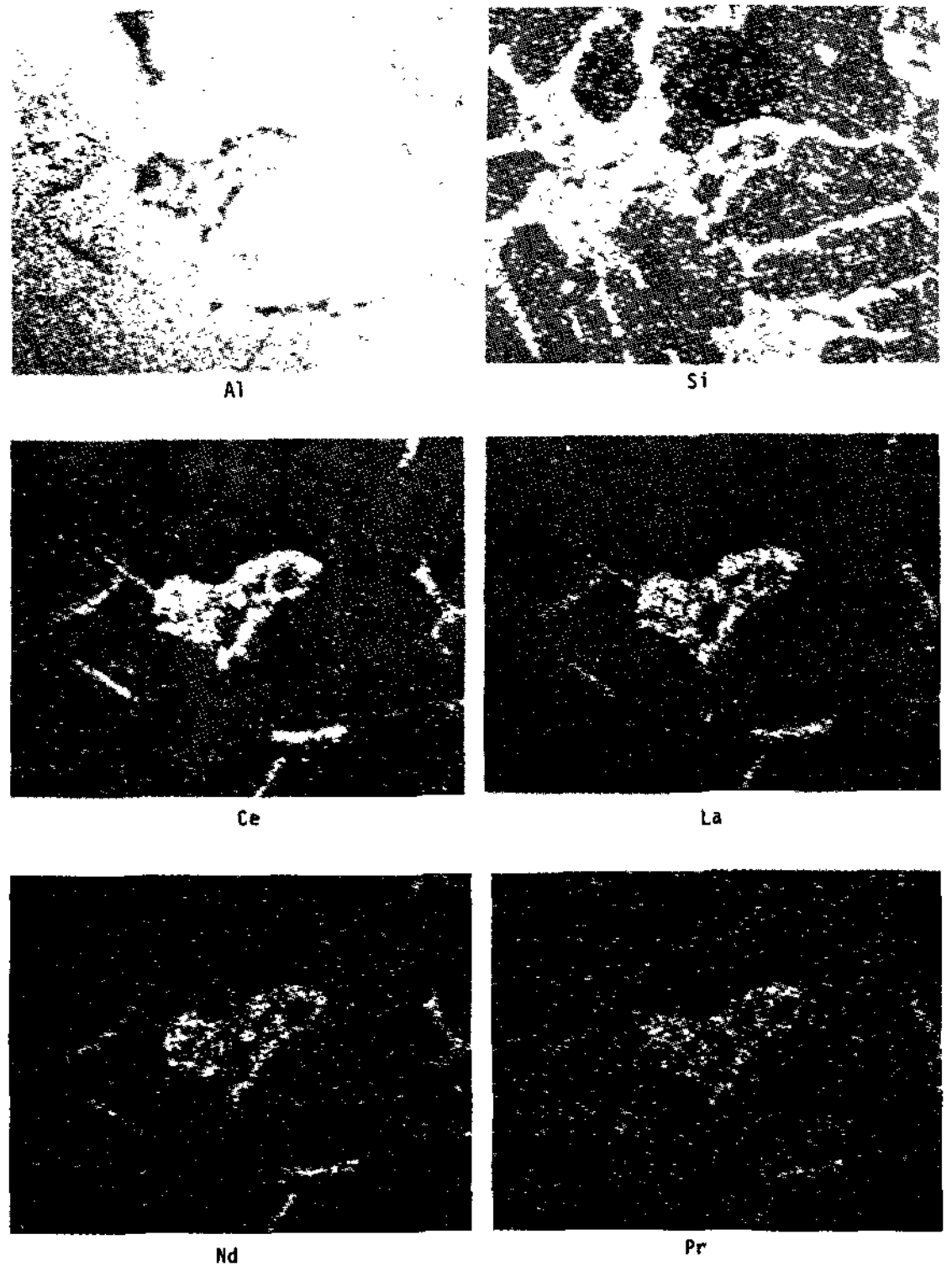
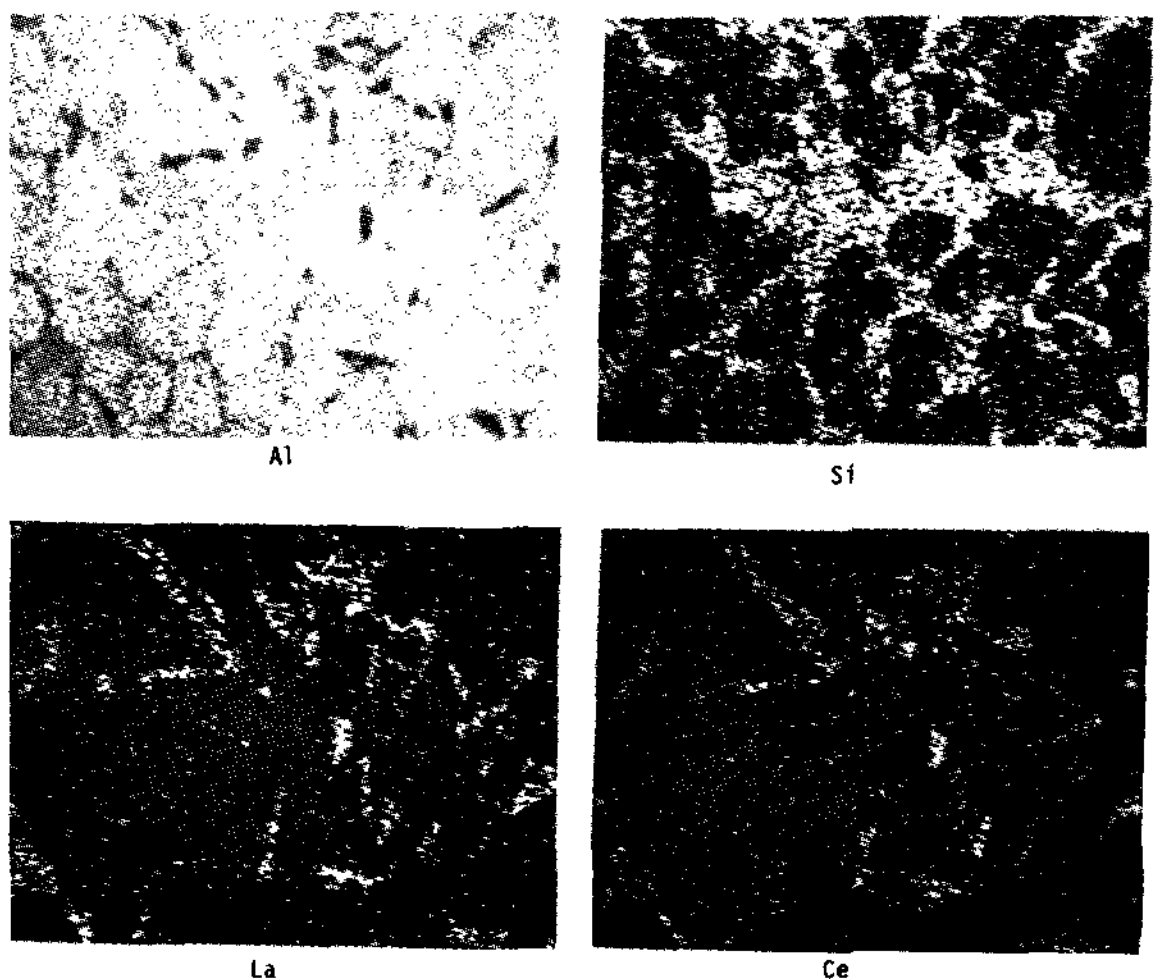


Fig. 11. Distribution of selected elements in the microstructure of 356 aluminum alloy modified with a 2.0% misch metal addition in a 0.75 in.D. sand mold cast 60 minutes after treatment. SEM. 360X.



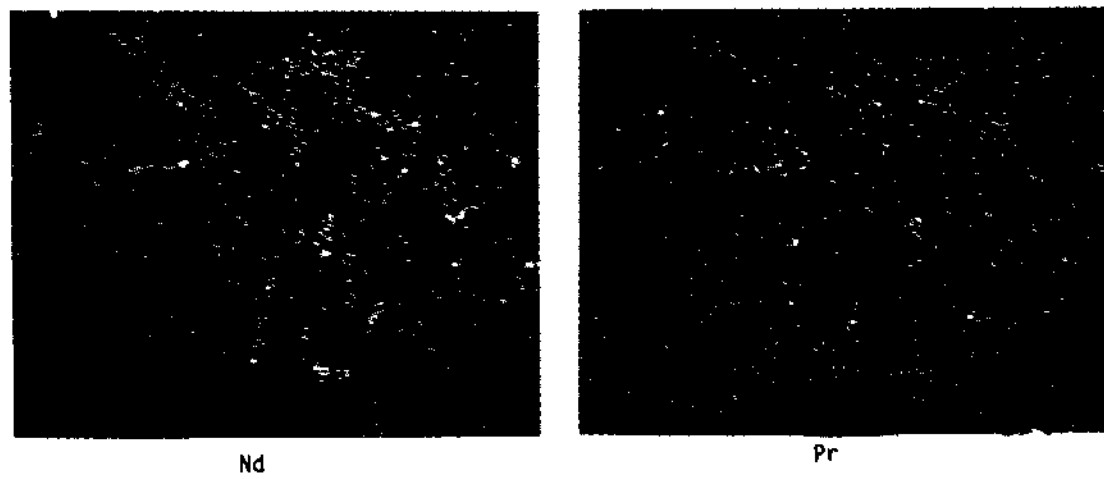


Fig.12. Distribution of selected elements in the microstructure of 256 aluminum alloy modified with a 2.0% misch metal addition in a 1.25 in.D. graphite mold cast 60 minutes after treatment. SEM, 360 X.

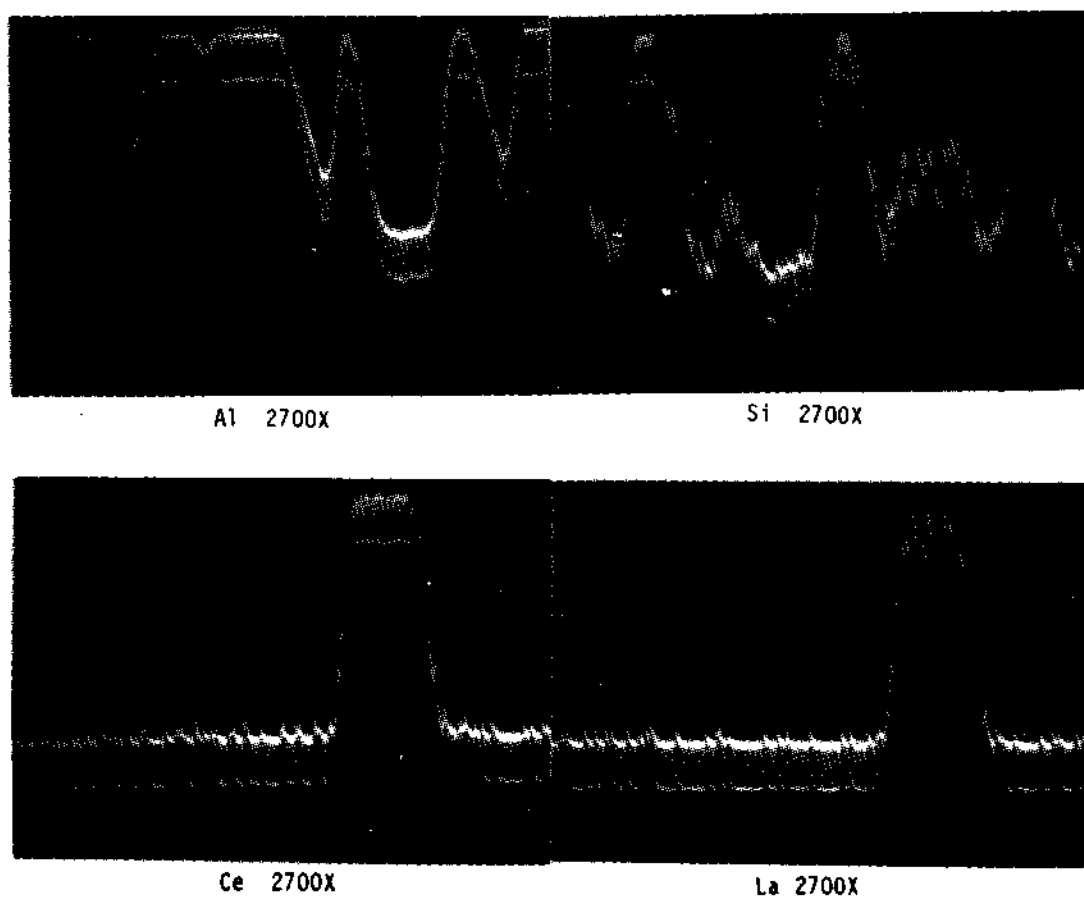
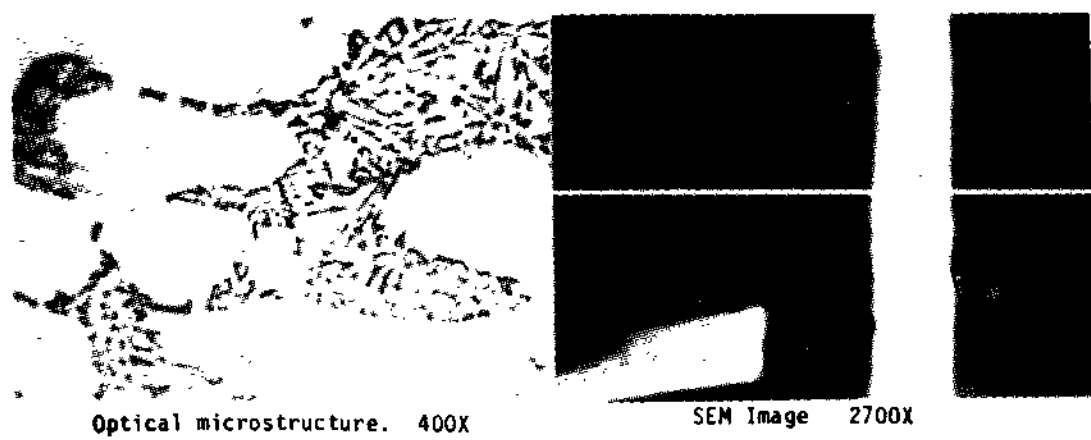


Fig.13. Distribution of selected elements in the microstructure of 356 aluminum alloy modified with a 2.0% misch metal addition in a 0.75 in.D. sand mold cast 60 minutes after treatment. Linear X-ray scan.

Table 4. Distribution of Selected Elements (Averaged) After Modification of 356 Aluminum Alloy with 2.0% Misch Metal

Cast into a 1 1/2 inch Diameter Sand Mold (Unit is wt %)

Elements/ Locations	$\alpha$ in eutectic	Si in eutectic	$\alpha$ -Si interface	Compound
Al	96.66	32.87	66.84	22.19
Si	2.79	66.72	32.65	21.58
Fe*	-	-	-	-
Mg*	-	-	-	-
Ce	.05	.04	.08	28.18
La	.02	.04	.05	15.94
Nd	.01	.05	.10	7.24
Pr	.01	.02	.02	4.29
MM Total	.08	.08	.18	55.65

\* Not recorded. The level in original 356 ingot is Fe = 0.18, Mg = 0.36.

Table 5. Distribution of Selected Elements (Averaged) After Modification of 356 Aluminum Alloy with 2.0% Misch Metal Cast Into a 1 1/4 inch Diameter Graphite Mold (Unit is wt %)

Elements/ Locations	$\alpha$ Primary	$\alpha$ in eutectic	Si in eutectic	Compound
Al	97.19	98.19	51.11	27.37
Si	1.90	1.42	49.57	18.90
Fe*	.11	.11	.10	.42
Mg*	.19	.26	.19	.58
Ce	.03	.02	.02	6.65
La	**	**	.01	15.20
Nd	.02	.03	.04	8.91
Pr	**	**	**	4.68
MM Total	.03	.03	.04	43.08

\* The level in original 356 ingot is Fe = 0.18, Mg = 0.36

\*\* Too small to detect.

a. Sand Molds

1. The rare earth elements do not show any segregation to either the aluminum or silicon phases in the eutectic. An average of 0.08% rare earth was detected in both of these phases.
2. Somewhat higher rare earth content was detected at the interface of the aluminum and silicon phases in the eutectic. In this region the rare earth content ranged from 0.10 to 0.28%.



3. The intermetallic compounds found in the structure of rare earth treated alloys were identified as  $\text{Si}_2\text{Al}_3\text{RE}$  and  $\text{AlSiFeRE}$  (where RE represents rare earths).

b. Graphite Molds

1. Only small amounts of rare earths are presented in the aluminum (0.03%) and the silicon (0.04%) phases of the eutectic structure.

2. The intermetallic compounds formed were identified as  $\text{Si}_x\text{Al}_y\text{RE}$ , where  $x=2.3-2.8$  and  $y=2.2-8.0$ , and  $\text{AlSiFeRE}$ .



Fig.14. Eutectic silicon phase extracted from a 2.0% misch metal modified 356 aluminum alloy cast into a 1.25 in.D. graphite mold. Transmission electron microscope.

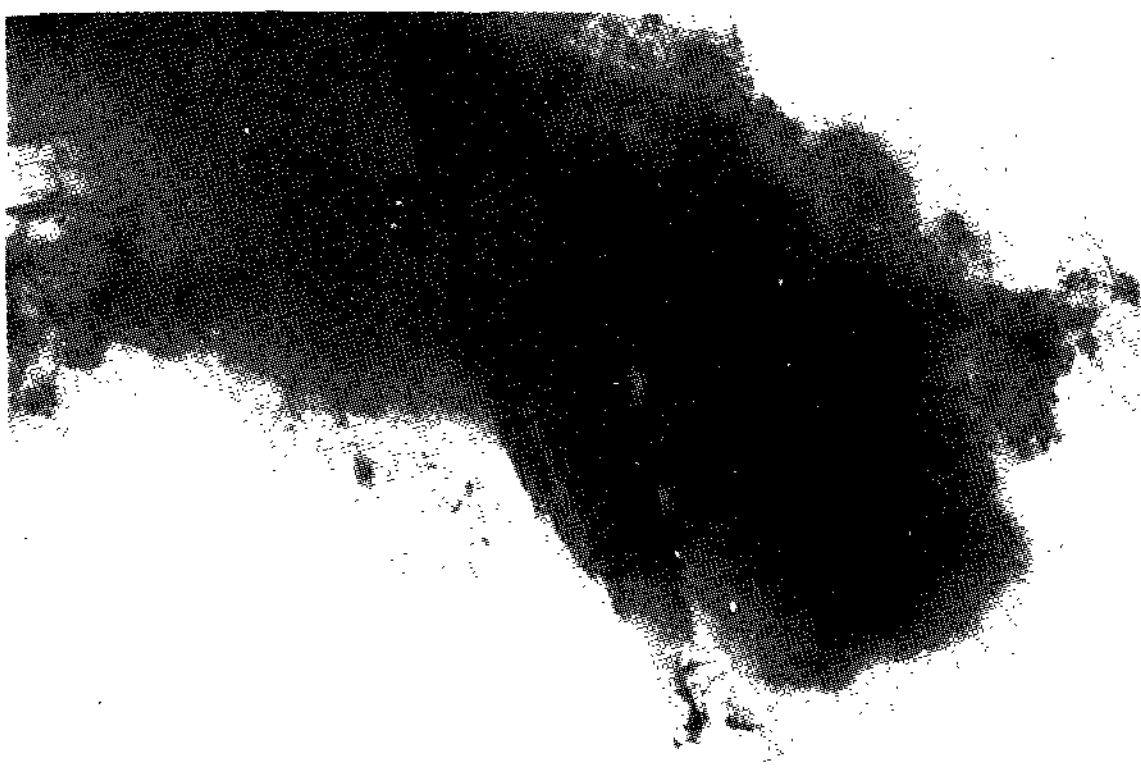


Fig.15. Eutectic silicon phase extracted from a 2.0% misch metal modified 356 aluminum alloy cast into a 1.5 in.D. sand mold. Transmission electron microscope.

The TEM photographs of Figures 15 and 16 indicate that the silicon phase in the eutectic grows in the  $\langle 100 \rangle$  direction. Crystal growth twins are evident.

#### 4. DISCUSSION

Even a cursory review of the data generated by this research indicates that while rare earths can be used to modify the eutectic structure of cast aluminum-silicon alloys, the amount of rare earth required to achieve modification is excessive, and the sufficiency of that modification is questionable. The rare earths, however, present another path to the understanding of the mechanism of eutectic modification in these alloys.

##### 4.1 Primary Alpha Aluminum Formation

Solidification of these hypoeutectic aluminum-silicon alloys begins with the development of alpha aluminum dendrites. Sodium or strontium treatment of the melt does not result in any noticeable change in the morphology of these dendrites, however, treatment of the melt with rare earths was observed to significantly affect the secondary dendrite arm spacing.

The reduction of secondary dendrite arm spacing as a function of solidification cooling rate was found to agree with the results of Spear and Gardner (26) for untreated, sodium and strontium treated aluminum alloys 319, 355 and 356, Figure 7. It is apparent, though, that a 2% mischmetal treatment effects a marked reduction in the dendrite arm spacing. (While measurements of the secondary arm spacing have not been recorded for all treatment levels, it appears that this effect is generally proportional to the amount of rare earths added.) It would seem appropriate to conclude that this is an alloying effect of the rare earths.

As a result there is a slight influence of the secondary arm spacing on the morphology of the eutectic silicon, since the interdendritic channels serve to restrict the growth of the eutectic silicon phase. This, however, is not a modification effect.

This solid solution alloying effect was not sufficient to result in an increase in the microhardness of the alpha aluminum phase, even with 2% rare earths added.

##### 4.2 Eutectic Undercooling

It is well recognized that the cooling curve can be used to characterize the solidification behavior of many alloys, including the modification of aluminum-silicon eutectic alloys. One investigation (14) concluded that a eutectic undercooling of 6 to 10°C (11 to 18°F) is necessary for appropriate modification in an alloy treated with 60 to 120 ppm sodium. An unmodified structure is obtained with less undercooling. In general, successful modification requires eutectic solidification at specific undercoolings (12, 16, 17).

The eutectic undercooling was shown to increase linearly with an increase in the amount of rare earth treatment (up to 2% rare earths), Figures 2, 4, 5 and 6. It was also demonstrated that modification using rare earths could not be achieved if the combination of solidification cooling rate and modifier were below certain levels, e.g., 2% rare earth for the 0.75 in. D. sand mold, and 1% rare earths for the 1.25 in. D. graphite mold.

The fading effect of sodium occurred quite rapidly after a 10 minute holding time, as seen by the decrease in the amount of eutectic undercooling. On the other hand, mischmetal treatment was quite resistant to fading, and produced greater levels of undercooling. With mischmetal treatment an increase in eutectic undercooling occurs up to 60 minutes of holding time, during which dissolution and distribution of the rare earths occurs. At longer holding times, it is likely that the rare earth levels in the melt are decreased due to oxidation.

Even though the eutectic undercooling obtained in rare earth treated sand cast bars was greater than that where modification was attained in sodium treated bars, the rare earth treatment did not lead to complete modification.

While it would be possible to document the modification process by counting the number of silicon particles in the eutectic structure, this procedure is difficult and tedious. Furthermore, while the silicon particles appear to be individual and discrete particles when examined under the optical microscope, the SEM shows that the silicon phase is interconnected in a rosette form, Figures 8 and 9, confirming the results of Day (18). By adding copper to an aluminum-silicon eutectic alloy, the eutectic cell size was reduced. However,

modification of the eutectic by sodium treatment of the melt did not result in a change in eutectic cell size.

Growth features of the silicon phase have been studied showing that the silicon plates grow twinned (20) and that a common type of defect structure is the reflection twin (19). Because of the lowest attachment kinematic energy on (111) in the diamond cubic system, the silicon crystals will grow from a defect. Extracted silicon plates have an approximately (111) habit and contain multiple twin traces (12, 21). The twinned boundaries enable the silicon to grow at small melt undercoolings. The observations of the transmission electron microscope demonstrate the existence of twinned silicon crystals.

Silicon crystals modified with rare earths grow in the  $\langle 100 \rangle$  direction, Figure 14. The morphology of the modified silicon phase is changed from faceted growth on (111) in  $\langle 211 \rangle$  directions (which leads to coarser plate silicon) to an  $\langle 100 \rangle$  orientation (which contributes to silicon crystals in a rod like form when misch metal is added). Misch metal can be observed to concentrate at the growing crystal surface and to likely poison the growth steps thus preventing the (111) faces from developing.

The electron microprobe analysis, Tables IV and V, show that the rare earth content of the alpha aluminum and silicon phases in the eutectic are about the same. Refinement of the aluminum-silicon eutectic has been attributed to the addition of small quantities of nucleating elements, such as titanium (11, 16) or phosphorus, where AIP nucleates silicon (23). Sharon (2, 3, 4, 5) attempted to describe modification in a similar manner. But there seems to be little in common between mischmetal compounds and compounds such as AIP, and no correlation of this effect with rare earths has been recorded.

High rare earth levels have been detected at the silicon and aluminum interface in the eutectic, Table IV, seeming to support the adsorption of rare earths on the growth front. It can be assumed that rare earths (or sodium) is absorbed on to the fast growing (111) face and effectively poisons the growth steps and prevents the (111) faces from developing (19, 22). Consequently, the silicon morphology changes. This mechanism, however, has not been proven and does not fully explain

the weaker effect of rare earth treatment compared to other modifying agents (e.g., sodium, strontium, etc.).

### 5. CONCLUSION

The effect of rare earths in the modification of the eutectic of cast aluminum-silicon alloys was investigated and the results were obtained as followed.

A reliable and persistent eutectic modification effect can be obtained with rare earth additions, however, the minimum amount of rare earths necessary to obtain proper modification is exceptionally large. The eutectic modification achieved through the use of rare earths is extremely resistant to fading and may persist up to several hours of holding time at temperature. In fact, due to the delayed solution of the rare earths in the melt, the amount of eutectic undercooling actually increases during the first 60 minutes or so after modification is obtained. As the rare earth addition level approaches 2%, some primary dendrite refinement (reduction in secondary dendrite arm spacing) becomes apparent. This is attributed to an alloying effect, and is not significant enough to be considered as a practical means of reducing secondary dendrite arm spacing.

The silicon phase modified by rare earths exhibits the same changes in crystallographic structure as achieved through modification with sodium. In both cases the silicon phase changes from growth in the  $\langle 211 \rangle$  directions, to growth in the  $\langle 100 \rangle$  directions where the silicon phase develops a refined, rounded and interconnected morphology.

The quantitative difference in modification effects of sodium and rare earths has not been fully determined, and is in need of further study.

Finally, it is apparent that the literature presents a misleading image as to the practical role of using rare earths to modify the eutectic structure of cast aluminum-silicon alloys. It is hoped that the results discussed in this work will permit this subject to be dealt with realistically.

### REFERENCES

1. G. K. Sigworth, *Theoretical and Practical Aspects of the Modification of Al-Si Alloys*, Reading Research and Development Laboratories, Cabot Corporation, 1983.
2. R. Sharan and T. R. Anantharaman, "Effect of Misch Metal Additions on the Properties of Aluminum and Its Alloys", *Trans. of the Indian Institute of Metals*, Vol. 17, June 1964, pp.89-93.
3. R. Sharan et al., "Modification of Aluminum-Silicon Alloys by Misch Metal Additions", *Current Science*, No. 21, Vol. 36, 1967, pp.568-570.
4. R. Sharan, "Influence of Rare Earth Additions on the Machinability and Mechanical Properties of Aluminum Alloys", *The 41st IFC*, No. 23, 1974, pp.29-33.
5. R. Sharan et al., "Rare Earth Additions as Modifiers of Al-Si Alloys", *AFS International Cast Metal Journal*, No. 1, Vol. 3, March 1978, pp. 29-33.
6. I. S. Hirschhorn, "Recent Applications of the Rare Earth Metals in Nonferrous Metallurgy", *Journal of Metals*, October 1970, pp.40-43.
7. Yoshizo Koike, et al., "The Properties of High Strength Aluminum Alloy for Electric Conductors", *Furukawa Denko Jiho*, No. 41, 1966, pp.9-16.
8. Kh. G. Vasilevskii, N. S. Postnikov and M. B. Al'tman, "Modification of Hypo-eutectic Silumin", *Russian Castings Production*, March 1973, pp.119-120.
9. C. B. Kim and R. W. Heine, "Fundamentals of Solidification in the Aluminum-Silicon System", *Journal of the Institute of Metals*, Vol. 92, 1963-1964, pp.367-376.
10. E. A. Boom, "On the Mechanism of Formation of the Structure of Modified Silumin", *Metallurgical Abstracts*, Vol. 20, 1952-53, pp. 81.
11. B. M. Thall and B. Chalmers, "Modification in Aluminum-Silicon Alloys", *The Journal of the Institute of Metals*, Vol. 77, 1950, pp.79-97.
12. A. Hellawell, "The Growth and Structure of Eutectics with Silicon and Germanium", *Progress in Materials Science*, Vol. 15, Part 1, 1970, pp.1-78.
13. Deyand Lu, B. J. Ye and Carl R. Loper, Jr., "Effect of La Addition on Microstructure of

- Cast Aluminum-Silicon Alloys”, to be published.
14. K. E. Honer, “Thermal Analysis Monitors Aluminum Modification or Grain Refinement”, *Foundary*, Oct. 1982, p.50-53.
  15. J. Charbonnier et al., “Thermal Analysis of Aluminum Alloys to Determine Their Suitability for Casting”, *AFS International Cast Metals Journal*, Sept. 1979, pp.39-44.
  16. R. C. Plumb and J. E. Lewis, “The Modification of Aluminum-Silicon Alloys by Sodium”, *Journal of the Institute of Metals*, Vol. 86, 1957-1958, pp.393-400.
  17. P. B. Crosley and L. F. Mondolfo, “The Modification of Aluminum-Silicon Alloys”, *AFS Trans.*, Vol. 74, 1966, pp.53-65.
  18. M. G. Day, “The Modification of Al-Si Eutectic Alloys by Metallic Na”, *Journal of the Institute of Metals*, Vol. 98, 1970, pp.57-59.
  19. I. Minkoff, “The Microstructure of Non-Metallic Phase in Metal, Non-Metal Systems”, *Crystal Growth*, AISI CIF, No. 9, pp.3-10.
  20. M. G. Day and A. Hellawell, “The Microstructure and Crystallography of Al-Si Eutectic Alloys”, *Proc. Royal Soc., Series A*, Vol. 305, 1968, pp.473-491.
  21. E. M. Pilarski, Ph. D. dissertation, University of Wisconsin-Madison, 1968.
  22. V. de L. Davies and J. M. West, “Influence of Small Additions of Sodium on the Surface Tension of Aluminum and Aluminum-Silicon Alloys”, *Journal of the Institute of Metals*, Vol. 92, 1963-66, pp.208.
  23. P. Borgeaud, et al., “Structure and Modification of Al-Si Alloys Close to the Eutectic”, *34th International Foundry Congress*, Oct. 1967, paper No. 4.
  24. Max Hansen, *Constitution of Binary Alloys* (New York, McGraw-Hill, 1958).
  25. L. F. Mondolfo, “Metallography of Aluminum Alloys”, *AFS Trans.*, Vol. 64, 1956, pp.693-697.
  26. R. E. Spear and G. R. Gardner, “Dendritic Cell Size”, *AFS Trans.*, Vol. 71, 1963, p.209-215.