Crystal Habits of Silicon Crystallized in Al-Si Alloys*

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Synopsis

Al-20 per cent silicon alloys containing none or only one of the following additional elements, viz. sodium, magnesium, zinc, chromium, manganese, copper, cadmium, tin, lead, antimony, bismuth, iron, nickel, and cobalt, were cooled very slowly or cast in sand molds. Then, the alloys were electrolized in hydrochloric acid solution by using lead-plate as the cathode. Silicon crystals thus obtained as the anode slime were collected and subjected to goniometry, X-ray and chemical analyses. From the above experiments, following three types of crystal habits of silicon have been detected: (1) Granular crystal, caused by addition of sodium and forming with {111} and {001} faces. (2) Prismatic crystal, caused by the addition of magnesium or zinc to the alloy and forming essentially with {111} face growing in the [011] direction. (3) Platy form crystal, which is most common and is formed in plain binary alloy or alloys containing one of the additional elements, chromium, manganese, copper, cadmium, tin, lead, antimony, bismuth, iron and cobalt, and forming with {111} faces in which one pair of the face {111} being parallel to each other is developed best. Although a small quantity of the added element was found to be contained in silicon crystals, no marked difference in the lattice constant has been found according to the crystal habit.

I. Introduction

It has been well known that when an inorganic substance crystallizes in aqueous or non-aqueous solution, different crystal habits are observed according to the difference in the crystallizing condition, such as some sorts of impurities contained in solution and the rate of crystal growth(1). Such a phenomenon is observed also in the cases of metal crystals grown in the liquid of an alloy. Since A. Pacz discovered that upon addition of a minute quantity of sodium, the eutectic structure of Al-Si alloy was modified, and that the mechanical properties of the alloy were improved, many studies have been reported on the subject. It is known that the silicon crystals primarily crystallizing in hypereutectic Al-Si alloys are spherodized by the addition of sodium and some other elements, but the former studies on the modification treatment of silumin have aimed at the improvement of its mechanical properties and at the mechanism of the modification of Al-Si alloys, none being concerned with the crystal habits of silicon grown in aluminium alloys. A. J. Goss(2) has made a crystallographical study of silicon crystallizing in Sn-Si system and reported that the silicon crystals growing in tin were formed only with {111} faces, which developed to the [011] direction.

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* The 870th report of the Research Institute for Iron, Steel and Other Metals.

(1) H. E. Buckly, "Crystal Growth" John Wiley & Sons Inc.

(2) A. J. Goss, J. of Metals, **5** (1953), 1085.

The present report represents the results of our experiments on the influence of the cooling rate and of the addition of one of the 14 elements including sodium, magnesium, etc. as the third element on the crystal habit of primary silicon crystals.

II. Experimental procedure

A master alloy containing about 25 per cent of silicon, as shown in Table 1, was prepared by alloying 99.5 per cent Al and crude silicon, and adding to it 99.98 per cent Al and 2 per cent each of various third elements, ca. 50 g of Al-20 per cent Si-2 per cent 3rd metal alloys were made. Two kinds of specimens, one by solidifying under a cooling rate of 1°/min., and the other by casting in dry sand molds, 20 mm in diameter, were prepared.

Table 1. Composition of crude silicon and Al-Si mother alloy.

Materials	Al	Fe	C	Ca	Si
Crude Si	0.29	0.31	0.093	0.31	Bal.
Al-Si alloy	Bal.	0.15	—	—	25.05

As the third element, one of the following 14 was used: sodium, magnesium, zinc, cadmium, tin, lead, bismuth, antimony, copper, manganese, iron, nickel, cobalt, and chromium. The last six elements were added in the form of master alloys.

These specimens were suspended in 3.5 per cent hydrochloric acid solution as anode, and by using a lead plate as a cathode they were subjected to electrolysis to dissolve aluminium, and the insoluble materials containing silicon were recovered as the anode slime, which was then treated with aqua regia and fluoric acid. Only the crystals that could be clearly discrimirated as primary silicon crystals were hand-picked from the residue for the following examinations.

From these samples of crystals, single crystals were searched out for the measurement of the plane angles with a two-circle reflection goniometer. The measured values were collated with the calculated values to determine the indices of the crystal planes. The best developed face was taken to be the polar plane, but in prismatic crystals, the direction of crystal growth was made to coincide with the direction of the horizontal axis. When a platy crystal was too thin for the goniometry, X-ray was used to measure the indices of the well developed plane. Chemical analysis was carried out to determine the quantity of impurities in the silicon crystals having different crystal habits, and their lattice constants were determined from their Debye-Scherrer patterns taken by the K_α ray of iron.

III. Experimental results

The primary crystals of silicon were observed as rarely single, but mostly of twin or aggregate type, and much less frequently of parallel growth. The primary silicon crystals extracted from binary alloy of Al-20per cent Si alloy were platy in form, but they turned granular by the addition of sodium, and prismatic by the addition of magnesium and zinc.

The influence of the added elements on the crystal habit of primary silicon crystals is shown in Table 2. Photos. 1 and 2 show the microstructures of slowly

Table 2. Habit-modifying character of the additional elements for the primary silicon crystal seperated from Al-20% Si alloy.

Crystal habits	Element added
Platy form	Bi, Cu, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sb, Sn
Prismatic form	Mg, Zn
Granular form	Na

cooled Al-20 per cent Si and Al-20 per cent Si-Na alloys, respectively. Even before isolating pure primary silicon crystals, we might as well observe herein that their crystal habits were varied.

On goniometry, the reflections from faces of silicon crystals were poor.

1. Granular form crystals

Photo. 3 shows a granular crystal of silicon extracted from a slowly cooled specimen of Al-20 per cent Si-Na alloy. The goniometrically measured values of the crystal, as shown in Table 3, agree well with the calculated values with (111)

Table 3. Measured and calculated angles for granular form crystal separated from Al-20% Si-Na alloy.

Angles measured		*hkl*	Angles calculated	
ρ	φ		ρ	φ
0	—	(111)	0	—
53°19′	0	(001)	54°44′	0
53°19′	118°25′	(010)	”	120°
53°19′	−120°03′	(100)	”	−120°
70°31	58°36′	$(\bar{1}00)$	70°32′	60°
70°33′	177°39′	$(11\bar{1})$	”	180°
70°43′	−58°36′	$(1\bar{1}1)$	”	−60

as the polar plane, in the table ρ standing for the polar distance and φ for the azimuth. Consequently, the crystal form of this crystal is deduced to be as shown in Fig. 1, being formed of the {111} and {001} faces. Such crystals were found more frequently in twin with {111} as the twinning plane. Photo. 4 shows the silicon crystals extracted from sand cast sample of Al-20 per cent Si-Na alloy. It was far

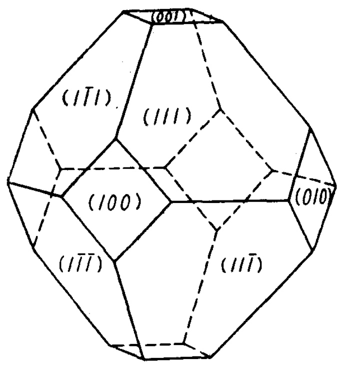

Fig. 1. Granular form silicon crystal grown in Al-Si alloy containing sodium.

smaller than the above, but all the crystal faces were also equally developed {111} and {001}.

2. Prismatic form crystals

Crystals showing this habit were observed in the specimens with added magnesium and zinc. Photo. 5 shows the crystals extracted from a slowly cooled specimen of Al-20 per cent Si-Mg alloy. The goniometrically measured values are shown in Table 4. As a good agreement of the above values with those calculated

Table 4. Measured and calculated angles for prismatic form crystal separated from Al-20% Si-Mg alloy.

Angles measured		*hkl*	Angles calculated	
ρ	φ		ρ	φ
35°55′	0	(111)	35°16′	0
90°56′	54°41′	$(\bar{1}11)$	90°	54°21′
90°57′	126°08′	$(\bar{1}1\bar{1})$	90°	125°39′
35°55′	180°0′	$(11\bar{1})$	35°16′	180°
90°0′	−123°43′	$(1\bar{1}\bar{1})$	90°	−125°39′
88°39	−54°22′	$(1\bar{1}1)$	90°	−54°21′

by taking (011) as the polar plane is observed, these crystals are formed of {111} and two pairs of {111} which are parallel to one another and are well developed to the [011] direction, as shown Fig. 2.

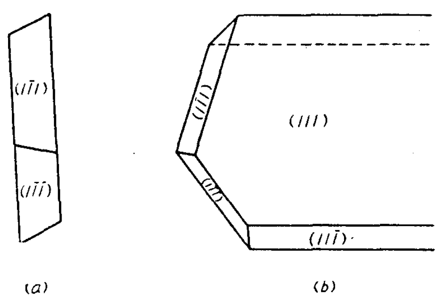

Fig. 2. Prismatic form silicon crystal grown in Al-Si alloy containing magnesium.
(a) Orthographic projection
(b) Clinographic projection

The crystals of this type were usually found in twins, with {111} as the twinning plane. The angles between the side faces were either 70° or 110°.

Photo. 6 shows the silicon crystals extracted from a sand cast alloy containing magnesium. The crystals were not always grown in prismatic form, but these having prismatic form were formed of {111} face alone developed to the [011] direction here too.

3. Platy form crystals

Crystals showing this habit were found, besides in the binary Al-Si system, in alloys containing cadmium, tin, lead, bismuth, copper, manganese, iron, nickel, cobalt, chromium or antimony. In the following, crystals extracted from Al-20 per cent Si binary alloys and from alloys containing chromium, manganese and antimony will be discussed as representative cases.

A photograph of silicon crystal extracted from the binary Al-20 per cent Si alloys is shown in Photo. 7. The thinness of the crystal of the platy form growth makes the measurement of the plane angle too difficult, so a Laue photograph was taken by X-ray striking the well developed face perpendicularly, as shown in

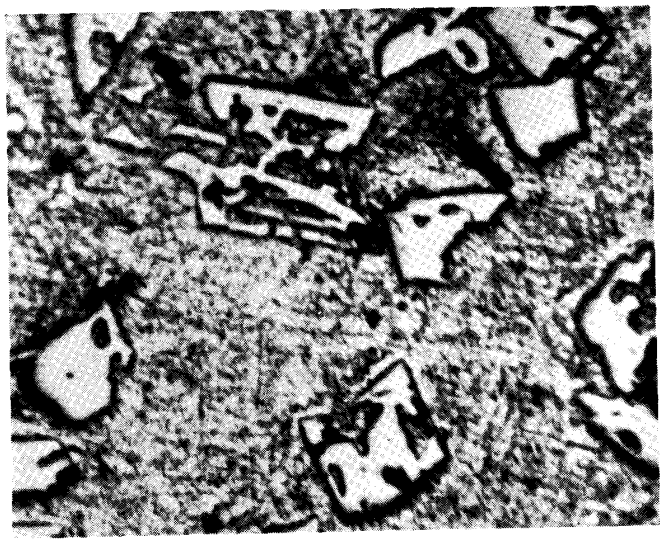

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Photo. 1. Microstructure of Al-20% Si alloy.

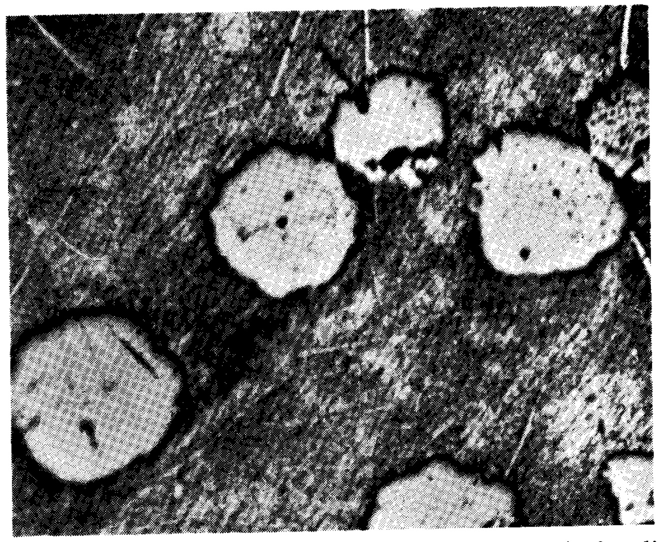

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Photo. 2. Microstructure of Al-20% alloy added 2% of sodium.

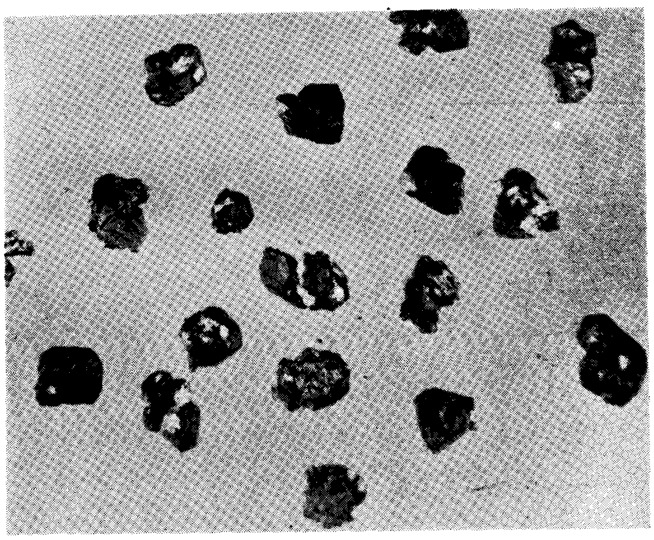

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Photo. 3. Crystals of silicon extracted from slowly cooled Al-20% Si alloy containing sodium.

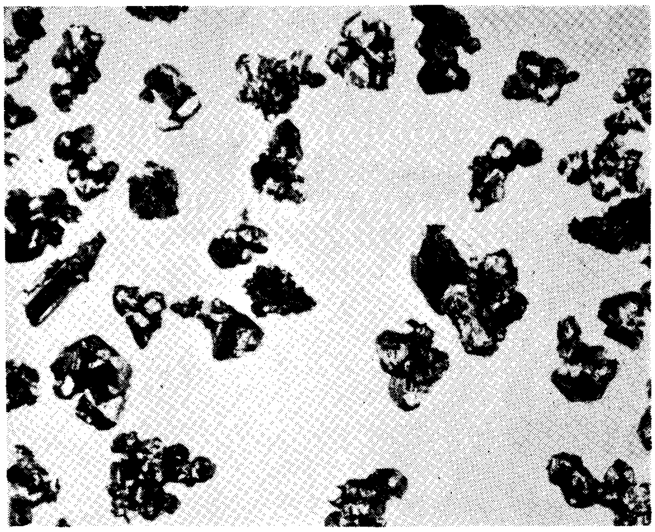

Photo. 4. Crystals of silicon extracted from sand cast Al-20% Si alloy containing sodium.

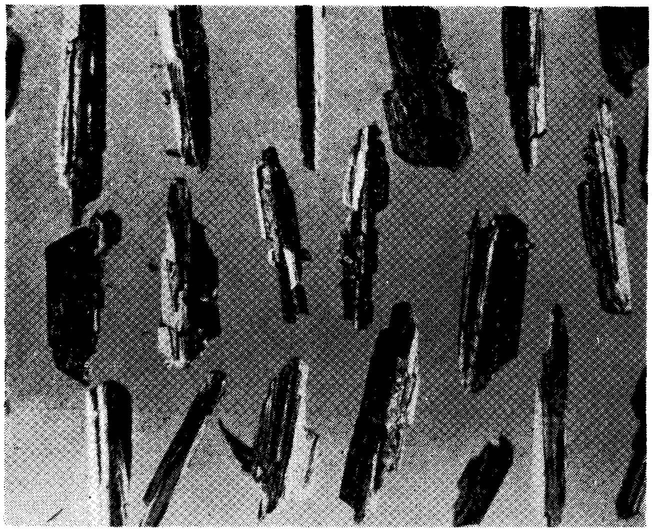

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Photo. 5. Crystals of silicon extracted from slowly cooled Al-20% Si alloy containing magnesium.

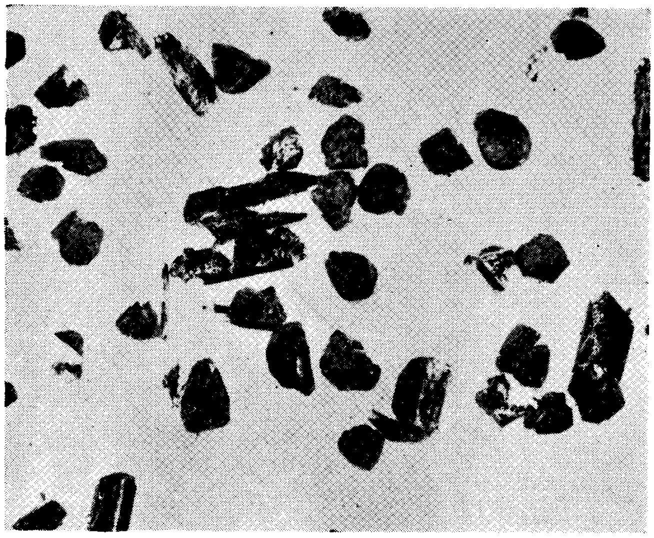

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Photo. 6. Crystals of silicon extracted from sand cast Al-20% Si alloy containing magnesium.

Photo. 8, in which the axis of trigonal symmetry clearly shows that the face of the crystal growth is that of {111}.

Photos. 9 and 10 show silicon crystals extracted from slowly-cooled alloys with added chromium and manganese, respectively. In these cases the measurement of plane angles was possible and the results are shown in Table 5. The measured values coincided with the values calculated with the

Table 5. Measured and calculated angles for platy form crystals separated from Al–20% Si–Cr alloy.

Angles measured		*hkl*	Angles calculated	
ρ	φ		ρ	φ
0		(111)	0	
71°47′	60°15′	($\bar{1}$11)	70°32′	60°
72°42′	180°12′	(11$\bar{1}$)	”	180°
71°44′	−59°58′	(1$\bar{1}$1)	”	−60°
55°11′	0	(1$\bar{1}\bar{1}$)	54°20′	0
55°18′	119°57′	($\bar{1}$1$\bar{1}$)	”	120°
55°35′	−120°18′	(1$\bar{1}\bar{1}$)	”	−120°.

{111} plane as polar plane, and the crystals with all the planes most uniformly developed (Photo. 10) would take the habit illustrated in Fig. 3. In the crystals extracted from Al-20 per cent Si alloy shown in Photo. 7, the planes (111) and ($\bar{1}\bar{1}\bar{1}$) were markedly developed, where as the planes (1$\bar{1}\bar{1}$), ($\bar{1}$1$\bar{1}$) and ($\bar{1}\bar{1}$1) were rather poor in growth, the angles between any two of the ($\bar{1}$11), (1$\bar{1}$1) and (11$\bar{1}$) planes being all 70°. The crystal showing hexagonal, as shown in Photo. 9, is a sample of such a crystal with all the side planes well developed. There were many twins among these crystals too, the twinning plane being, hard to determine.

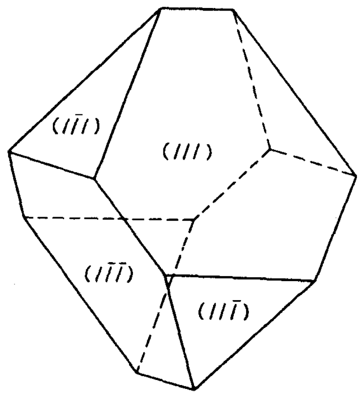

Fig. 3. Platy form silicon crystal grown in Al-Si alloy containing manganese.

Table 6. Measured and calculated angles for parallel growth crystal separated from Al–20 % Si–Sb alloy.

Angles measured		*hkl*	Angles calculated	
ρ	φ		ρ	φ
54°22′	45°0	(111)	54°45′	45°
54°18′	98°57′			
55°21′	136°13′	(1$\bar{1}$1)	54°45′	135°
56°41′	−170°43′			
56°45′	−133°45′	($\bar{1}\bar{1}$1)	54°45′	−135°
57°20′	−81°43′			
56°47′	−45°25′	($\bar{1}$11)	54°45′	−45°
55°39′	7°37′			

The crystals shown in Photo. 11 and extracted from a slowly-cooled alloy with added antimony showed the so-called parallel growth. The goniometrically measured values of the crystal are shown in Table 6. A set of values for four planes agreed well with the value for {111} calculated with (001) plane as standard. The planes of another set were in the positions turned 53° around [001] axis, but the indices of these planes were hard to determine. The habit of this crystal, as shown in Fig. 4, was that of a crystal developed with the {111} face developed also to the direction of [001].

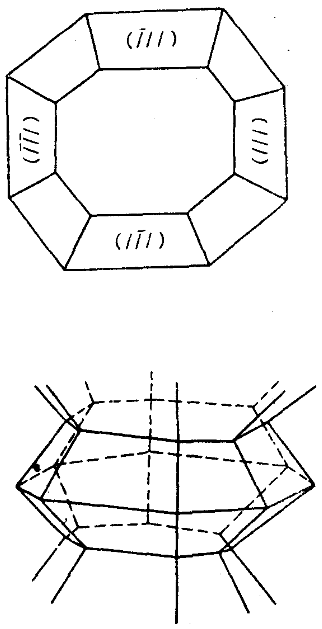

Fig. 4. Parallel growth crystal of silicon grown in Al-Si alloy containing antimony.

Photo. 12 shows the crystals extracted from a sand cast binary Al-20 per cent Si alloy. Quite as the crystal from the slowly-cooled alloy, it was in the form of a plate developed with the {111} plane. In the sand cast alloys containing antimony, no such parallel grown crystal as found in the slowly-cooled alloy was observed.

In Table 7, the results of chemical analysis of silicon crystals extracted from alloys of Al-20 per cent Si-Mn, Al-20 per cent Si-Zn, and Al-20 per cent Si-Na are shown. The sodium content could not be quantitatively determined, but a minute quantity of the added third element might be contained in the crystals.

Table 7. Composition of the silicon crystals having platy, prismatic and granular form, separated from Al-20% Si-2% Mn, Al-20% Si-2% Zn and Al-20% Si-2% Na alloy respectively.

Crystal habits	Al	Fe	C	others
Platy form	0.24	0.002	0.013	Mn = 0.008
Prismatic form	0.31	0.003	0.008	Zn = 0.050
Granular form	0.28	0.007	0.028	Na

The Debye-Scherre photographs of crystals of any of the habits showed the same diffraction pattern as the diamond type, and the lattice constants were all in agreement within the range of errors.

From the above results, it is clear that by adding specific impurities, the primary silicon crystals show various crystal habits. It is not clear, however, whether the mechanism of this change is due to a change in the physico-chemical properties of the molten alloy or an adsorption of the added elements on some specific faces of the growing crystal.

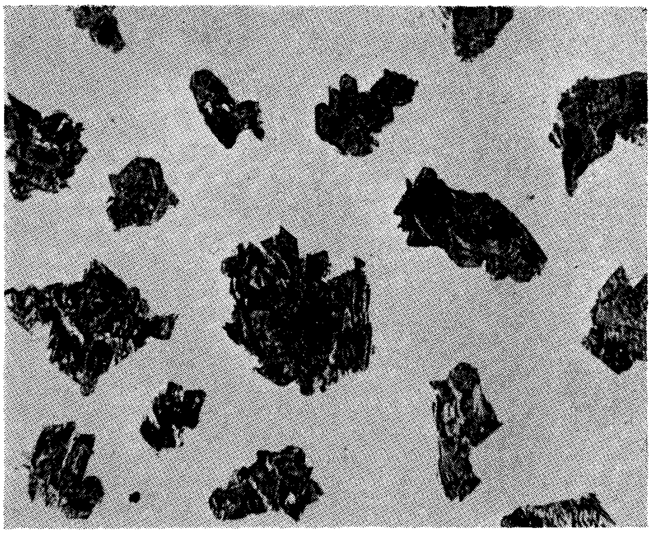

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Photo. 7. Crystals of silicon extracted from slowly cooled Al-20% Si binary alloy.

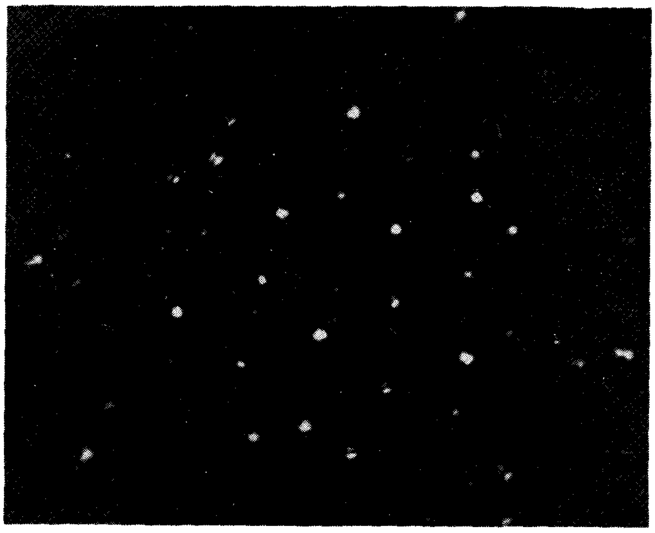

Photo. 8. X-ray Laue photograph of the platy form crystal of silicon obtained from Al-20% Si alloy.

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Photo. 9. Crystals of silicon extracted from slowly cooled Al-20% Si alloy containing chromium.

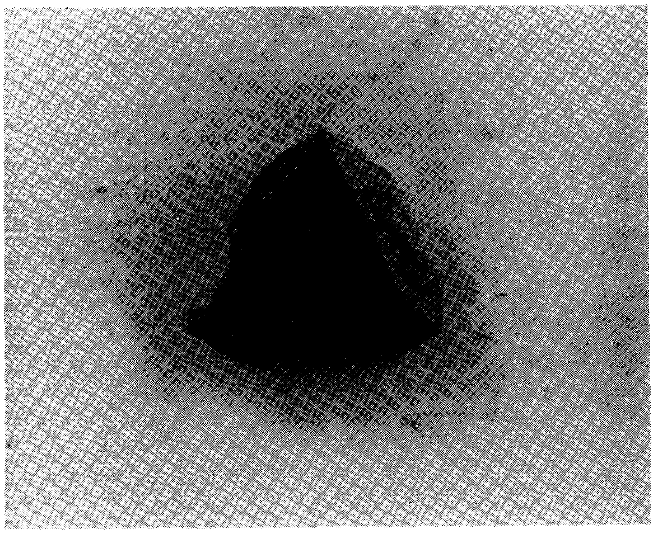

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Photo. 10. Crystal of silicon extracted from slowly cooled Al-20% Si alloy containing manganese.

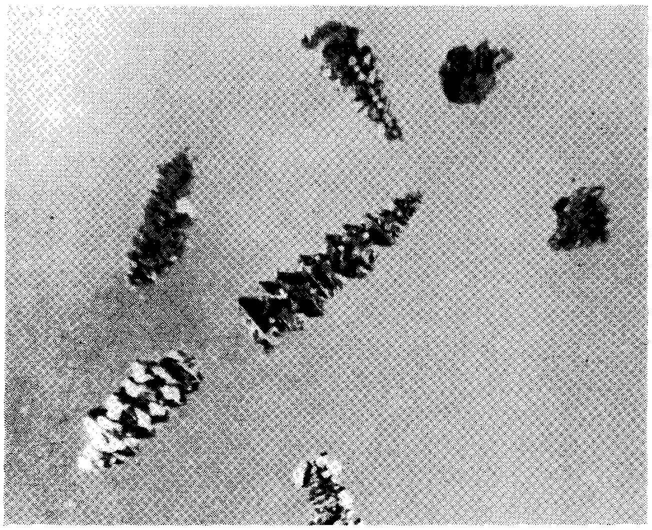

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Photo. 11. Crystals of silicon extracted from slowly cooled Al-20% alloy containing antimony.

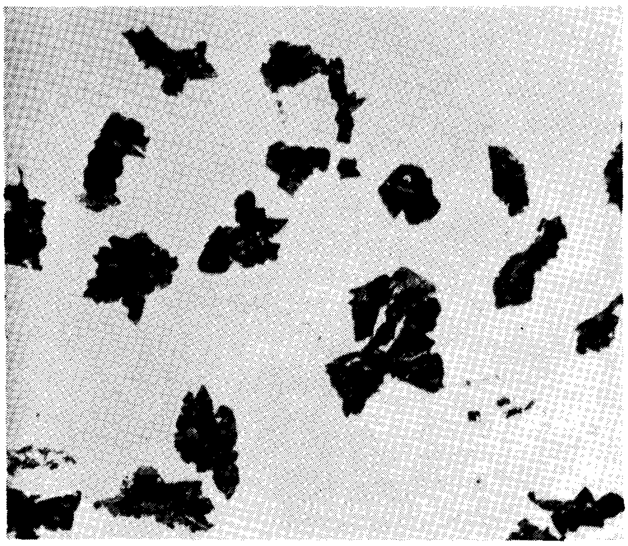

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Photo. 12. Crystals of silicon extracted from sand cast Al-20% Si alloy.

The spherodization of the primary silicon crystals in Al-Si alloys upon addition of sodium as shown in Photo. 2, is caused by the fact that the silicon crystals take the form shown in Fig. 1 with more different kinds of planes developed uniformly than in platy form crystals.

Summary

The results of present studies on the influence of the addition of a third element on the crystal habit of silicon crystallized primarily in Al-Si alloys have led to the following conclusion.

Silicon crystals grown in the binary alloy are platy formed by developing a pair of the {111} planes, which are parallel to each other. The same form is observed upon addition of copper, cadmium, lead, bismuth, iron, nickel, cobalt or chromium, but when manganese is added, the {111} planes undergo uniform growth, while in an antimony bearing alloy silicon crystals are observed to form parallel growth crystals.

In alloys containing sodium, the silicon crystals take the form of isotropic granules by growing uniformly two sorts of planes {111} and {001}.

The silicon crystals formed in alloys containing magnesium and zinc tend to become prismatic, formed with {111} planes developing to the direction of [011].

There was little difference between the habits of the crystals extracted from slowly-cooled and sand cast alloys, and it is inferred that the difference of this order in the cooling rate does not affect the habits.

In the primary crystals of silicon is contained a minute quantity of the added element, but the lattice showed nearly no change despite the difference in the crystal habit.

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