

TITLE:

Investigation of Ternary Aluminium Alloy Systems : AI-rich Al-Fe-Si System

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Investigation of Ternary Aluminium Alloy Systems. Al-rich AI-Fe-Si System.

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Since commercial aluminium always contains iron and silicon in measurable quantities as its chief impurities, it might be rather called an Al-rich Al-Fe-Si alloy. The constitutions of this alloy system has not yet been thoroughly investigated, however, and the present research has been carried out to ascertain it.

ALUMINIUM-IRON SYSTEM.

The binary alloy system of aluminium and iron has been investigated by many authors, such as Roberts-Austen¹⁾, Kurnakow, Urarow and Grigoriew², Gwyer and Phillips³, Murakami and Izawa⁴, etc. Rosenhain, Archbutt and Hanson⁵⁾ carried out a research on the aluminium side, and found the existence of a eutectic point at 2% of iron. According to Dix, however, this eutectic point exists at 655 °C, the percentage of iron being 1.7%, and iron is not at all soluble in aluminium. As the investigation of Dix is considered to be the most accurate, we did not think it necessary to go over the ground covered by him in this research.

ALUMINJUM-SILICON SYSTEM.

The binary system of aluminium and silicon has been investigated by Fraenkel⁶, Rosenhain, Archbutt and Hanson⁷, Edward⁸, Otani⁹, etc.

t) Roberts-Austen: Proc. Inst. Mech. Eng., (1895).

²⁾ Kurnakow, Urasow, Grigoriew: Z. anorg. Chem., 125 (1922) 207.

³⁾ Gwyer, Phillips: J. Inst. Metals (1927).

⁴⁾ Murakami and Izawa: Kinzoku-no-kenkyu. 2 (1925) 751.

⁵⁾ Rosenhain, Archbutt, and Hanson: Eleventh Report of Alloy Research Committee of Mechanical Engineers.

⁶⁾ Frankel: Z. anorg. Chem., 58 (1908) 154.

⁷⁾ Rosenhain, Archbutt, Hanson; Op. cit.

⁸⁾ Edwards: Chem. & Met. Eng., 28 (1923) 165.

⁹⁾ Otani: Kinzoku-no-kenkyu, (1921) 212.

C. Hisatsune¹¹ of our laboratory has also published a report on this system. In his research he found that a eutectic point between Al and Si exists at 11.6% of silicon and temperature 578° C. These results coincide well with those of Edwards, Dix and others.

The solid solubility of silicon in aluminium has been also determined by Gwyer and Phillips², Otani, Köster and Müller³, Dix and Heath⁴. The results of these researches are summarized in Table I.

Temp.	Otani	Gwyer	Köster	Dix
577		1.60	1.69	1.65
550	1.45	1.35	1.57	1.30
500		0,90	1.17	0.8 _O
460	0.95			
450			0.83	0.48
400			0.50	0.20
350			0.25	0.17
300			0.10	0.10
200	\sim \sim			0.05

Table 1.

Thus the results of these investigations are almost in accordance with one another, and we therefore found it unnecessary to investigate this part of the subject again.

IRON-SILICON SYSTEM.

Many investigations^{$5)$} have been published on the iron-silicon alloy system, and its equilibrium diagram is almost completely established. As this system was not directly necessary in our present investigation, we took

¹⁾ Hisalsune: Suiyokwai-shi, 4 (1925) 456.

²⁾ Gwyer, Phillips: J. Inst. Metals, 36 (1926) 283.

³⁾ Köster, Müller: Z. Metallkunde, 19 (1927) 52.

⁴⁾ Dix, Heath: Am. Inst. Min. Met. Eng. Metal Division, (1928) 164.

⁵⁾ Guertler, Tammann: Z. anorg. Chem. 47 (1905) 163.

Goutermann: Op. cit. 59 (19o8) 384.

Sanfourch: *Rev.* Metallurgie, 16 (1919) 217.

Bogdau: Bulletin de la societe de Chemie de Roumaine, **1** (1919) 6o ..

Murakami: Science reports of Tohoku Imp. Univ. 10 (1921) 79! 16 (1927) 475. Kurnakoff, Urazoff: Z. anorg. Chem. 123 (1922).

into consideration only the existence of a compound FeSi₂ on the silicon side of this system; this compound is considered by Haughton and Becker¹¹ to be $Fe₂Si₅$, in which opinion they are at variance with the other investigators.

ALUMINIUM-IRON-SILICON SYSTEM.

Merica, Waltenberg and Freemann²⁾ made an investigation on commercial aluminium and found that a ternary compound of Al-Si-Fe existed. This they called X . According to Wills³), this compound has the characteristics to be present in Chinese script.

With regard to the equilibrium diagram, Rosenhain, Archbutt and Hanson⁴ published an account of their research on the alloys containing up to 8% of Si and up to 8% of Fe. Gwyer and Phillips⁵⁾ studied this ternary system within the range of $0-30%$ of Fe and $0-15%$ of Si. Their so-called " meta-stable diagram", however, may be said to be difficult to understand.

Dix and Heath⁶⁾ investigated the alloys heated for r to ζ weeks at 560°C and found two kinds of compounds which they called α and β . One of them was said to correspond to *X*. From the results of *X*-ray analyses, Fink and Horn^{τ_j} concluded that this one showed almost the same space lattice as that of FeAl, and that β was a ternary compound having a different lattice from the former.

Recently Fuss⁸¹ reported that *X* was the compound $Al_6Fe_2Si_3$, and that a ternary eutectic point among Al, Si, and this compound existed at 570°C, its composition being 12.5% of Si, 0.5% of Fe and 87% of Al.

His explanation of the equilidrium dagram is either incomplete or

- **1)** Haughton, Becker: J. Iron and Steel Inst. **121** (1930) 315.
- 2) Merica, Waltenberg Freemann: Trans. Am. Inst. Min. Met. Eng. 64 (1920) 3.
- 3) Wills: Metal Industry (London), (1919).
- 4) Rosenhain, Archbutt, Hanson: Op. cit.
- 5) Gwyer, Phillips: J. Inst. Metals, 38 (1927) 29.
- 6) Dix, Heath: Am. Inst. Min. Met. Eng. Metal Division, (1928) 164.
- $7)$ Fink, Horn: Op. cit. (1929).
- 8). Fuss: Z. Metallkunde, 23 (1931) 231.

impossible to understand from the theoretical standpoint.

In a word the investigations hitherto carried out have not comptetely elucidated the constitutions of Al-rich Al-Fe-Si alloys or those of commercial aluminium. The purpose of the present research was therefore to determine the equilibrium diagram of the Al-rich Al-Si-Fe system.

MATERIALS EMPLOYED AND PREPARATION OF SPECIMENS.

The materials employed were aluminium 99.6% pure, Armco iron and metallic silicon 98% pure. Specimens were prepared from these materials, and after analysis they were used for thermal analyses or microscopical study after proper heat treatment.

EXPERIMENTAL METHOD.

The method of differential thermal analysis was employed to take the cooling curves during solidfication, and the specimens heated at various temperatures and quenched in water were examined under the microscope.

Fig. I shows the arrangement for the differential thermal analysis adopted in this investigation. A porcelain tube a, of which the lower end was closed and the upper end was cooled by a water-jacketed brass ring δ ,

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was placed in a nichrome-wound electric furnace; d is a small Tammann crucible in which the previously prepared specimen was inserted. The difference in temperature between the specimen and a piece of nickel placed above the crucible, and the temperature of the specimen, were measured during cooling from a temperature higher than the melting point of the specimen with a thermo-couple which is the same as the one in Saladinle Chatelier's apparatus. During this measurement, the tube a was kept in vacuo by means of a vacuum pump connected to it at the brass ring δ . Thus the differential cooling curve of the specimen was obtained.

RESULTS OF THERMAL ANALYSES.

Measurements were made for the alloys corresponding to the compositions of the constitutional sections 1% , 2% , 4% , 10% , 15% , 20%, 25% and 32% of iron and containing up to 30% of silicon. The results of the experiments are shown in Table 2.

No.	Composition (by analysis) %			Point of change or arrest ^o C.		
	Fe	Si	Aĺ			
Αı	1.38	1.53	Remainder	642	622	
A $\boldsymbol{2}$	1.41	2.37	,,	642	610	578
A 3	1.32	4.47	,,	637	614	577
A $\overline{4}$	1.41	5.63	,,	625	614	577
A 5	1.23	6.78	,,	621	602	577
A 6	1.24	7.63	,,	616	598	578
A 7	1.26	9.56	,,	612		578
A 8	1.28	12.30	,,	590		578
A ₉	1.27	14.78	,,	590		579
AIO	1.37	16.63	,,	620		578
AH	1.23	24.97	,,	735		578
A12	1.37	31.45	,,	790	583	578
Bи	2.05	1.56	,,	643	611	
B $\boldsymbol{2}$	2.03	2.51	,,	644	611	578
В 3	2.13	3.71	,,	641	611	578
B $\overline{4}$	1.96	4.87	,,	631	610	578
В 5	2.02	6.08	,,	619	611	577
B 6	1.99	7.04	,,	613	610	577
B 7	2.03	8.34	,,	608		578
В 8	2.03	10.66	,,	600		578
в \overline{Q}	1.75	13.23	,,	584		578
B10	1.85	14.20	,,	582		578
B11	1.59	17.46	,,	622		577
$_{\rm B12}$	2.01	26.26	,,	755		578
B_{13}	2.12	31.77	,,	875	655	578

Table 2.

 $\sim 10^{-10}$

$T_{\text{old}}(a)$ (Centinued)

 $\label{eq:2} \frac{1}{\sqrt{2}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{\sqrt{2\pi}}\sum_{i=1}^n\frac{1}{$

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this temperature 578°C coincides with the eutectic temperature of the binary system of aluminium and silicon, it must be the same reaction as

Liquid \rightleftarrows (Al)+Si

in the Al-Si binary system, where (Al) denotes Al-rich solid solution. Therefore, we may conclude that the ternary eutectic point given by Fuss does not exist in this system.

The results of microscopical study being also taken into consideration the results of the thermal analyses were plotted on the sectional diagrams as shown in Figs. 2-9, and Figs. 10-18 show the constitutional sections corresponding to 2%, 4 *o/o* , 6 *o/o* , 8 % , IO *o/o* , I 5 *o/o* , 20 *o/o* , 2 5 ~0 and 30% of silicon which were derived from the above sections. The liquidus surfaces are illustrated in Fig. 19.

From these diagrams we observe that three invariant reactions exist in the domain of our investigation. One of them occurs at 578°C, and it is found in every section. As

Liquidus Surfaces

Another invariant reaction is observed to exist at 615° C and near the side of the Al-Fe system. This reaction was observed by Rasenhain,

Archbutt, and Hanson, although the nature of it was not ascertained. From our experiments, however, this reaction can be shown to be a peritectoeutectic reaction

Liquid + FeAI₃ \Rightarrow FeAl₃·FeSi₂ + (Al)

where the ternary compound $FeAl₃·FeSi₂$ corresponds to the compound known as X , the formula of which has not been determieed hitherto except by Fuss. The present writer proved microscopically the reason why this compound is represented by $FeAl₃·FeSi₂$, as described later; it is indicated by *T* in· the Figures.

Furthermore, an invariant reaction is found to occur at 870° C as shown in the sectional diagram of 32% of iron. In the present investigation its true nature could not be determined, but it is probably a peritectoeutectic reaction

Liquid + $\chi \geq$ FeAl₃+ FeAl₃·FeSi₂

where χ denotes an unknown phase.

. **MICROSCOPICAL STUDY.**

In our microscopical examination, etching was done with a dilute water solution of hydrofluoric acid, as Gwyer and Phillips recommended. By this method $FeAl₃$ and $FeAl₃·FeSi₂$ were both coloured brown, but they were distinguished from each other by a defference in the slude of the colour. In cast pieces the needle-like crystals of FeAl₃ were sometimes found to be enveloped by $FeAl₃·FeSi₂$ in consequence of the peritectic reaction

Liquid + FeAl₃ \rightleftarrows FeAl₃·FeSi₂.

In such cases long annealing was needed for equilibrium of structure to be attained. Consequently these crystals were etched in various shades of colour accord:ng to the degree of the progress of the reaction and even the same crystal of the ternary compound was coloured from brown to blue according to the degree of the etching. This may be the reason why Gwyer and Phillips supposed that there were many meta-stable phases, even if there existed only one ternary compound.

Reduced to $\sqrt[3]{4}$

 (13)

 \sim

 $\frac{1}{\sqrt{2}}$

 (14)

 (15)

 (16)

 $\hat{\mathbf{x}}$

Reduced to $3/4$

Some examples of micrstructures are shown in Photos r-r6. Photo. I shows a microstructure of specimen A1 (Fe 1.38%, Si 1.54%) which was heated for two hours at 600°C and quenched in water. In the matrix of (Al) there are two kinds of needee_-like· cryst_als indicated by *a* and b; both of which are seen under the microscope to be coloured brown; and the slightly lighter-coloured crystals are $FeAl_s(a)$ and the deep coloured ones are $FeAl_3\text{-}FeSi_2$ (b). This heating time of two hours was too short for equilibrium to be attained. If equilibrium is attained, the $FeAl₃$ should be transformed entirely into $[FeA]_3$ ^{$[FeSi_2$}. This is proved in the microstructure of the same specimen which was heated for two weeks at 250° C, as shown in Photo. 2.

Photo. 3 illustrates a microstructure of specimen A2 (Fe 1.41% , Si 2.37%) which was quenched at 250°C after being heated for two weeks. The long dark-coloured crystals are $FeAl₃·FeSi₂$ and the small light crystals are silicon, the latter being always observed to be greyish- blue under the microscope.

Photo. 4 represents a microstructure of specimen A3 (Fe $r.32%$, Si 4.47%) which was quenched at 605°C, i.e. the temperature at which liquid, (Al) and FeAl₃·FeSi₂ coexist as is seen in the sectional diagram. That is evident in this Photo.: the FeAl₃·FeSi₂ crystals are distributed along the boundaries of the primary crystals (Al) and the dark parts surrounding these . crystals are the liquid portion in which we see small dendritic crystals of (Al) which were produced during the rapid cooling by quenching. A similar structure found in specimen A5 (Fe 1.23%, Si 6.78%) quenched at 60° C is shown in Photo. 5.

As is shown in the Photo., the same specimen A5 annealed for 20

hours at 500°C and quenched at that temperature gave a similar structure to that of Photo. 3, differing only in containing many crystals of silicon.

Photo. *j* illustrates the microstructure of specimen B1 (Fe 2.05%, Si 5.6%) heated for two weeks at 250°C and quenched, in which $FeAl₃$ and $FeAl₃·FeSi₂$ are distributed in the matrix of (Al). When the specimen B2 (Fe 2.03%, Si 9.65%) was heat-treated in the same way, we observed that it consisted of the ternary compound and (A) , although the microstructure

is not shown in this paper. Such variations of co-existing phases were taken into consideration in drawing the sectional diagrams.

The microstructure of specimen D2 (Fe 10.43%, Si 1.95%) which was heated for 22 hours at 530°C and quenched in water is shown in Photo. 8, where it is seen that the primary crystals of $FeAl_s$ are enveloped by the ternary compound. The alloy containing 10.50% of Fe and 3.03% of Si shows the microstructure consisting of $FeAl₃·FeSi₂$ and (Al) as we see in Photo. 9: but, specimen D4 (Fe 10.55%, Si 4.36%) similarly heat-treated shows the structure consisting of silicon and $FeAl₃·FeSi₂$ on the (Al) matrix.

Photo. II represents the microstructure of specimen F1 (Fe 18.94% , Si 2.23%) heated for 25 hours at 250°C and quenched in water. In this figure we see also the phenomenon of the envelopment of $FeAl₃$ by $FeAl₃$ $F \in Si₂$ due to the reaction Liquid + $Fe Al₃ \rightarrow Fe Al₃ \cdot FeSi₂$.

In Photo. 12 we see the microstructure of F_4 (Fe 21.22%, Si 8.61%) heat-treated in the same manner. It can be seen that many needle-like crystals of the ternary compound are distributed in the matrix. Among them the larger crystals are the primary ones tranformed from FeAl3 into FeAl₃-FeSi₂ by the above-described peritectic reaction, while the smaller ones are the crystals produced during the secondary crystallization.

Photo. 13 represents the microstructure of F6 (Fe 20.91%, Si 12.14%) in which the enveloping of ternary compound on FeAl₃ is evident, but these enveloped crystals must be transformed into the ternary compound by longer heating. In this figure we also see small crystals of silicon and the ternary compound produced by the secondary crystallization.

Photos. 14 and 15 show respetively the microstructures of H₃ (Fe 32.18%, Si 19.90%) and H4 (Fe 31.95%, Si 22.90%); the former was heated for 20 hours at 515° C and quenched, and the latter was heated for 60 hours at 535°C and quenched. In these figures we see plainly the large crystals of enveloped ternary crystals in the matrix of (Al) and Si, i.e. these figures do not show any hornogeniety of structure. if a ternary compound $Al_6Fe_2Si_3$ (Fe 31.3%, Si 34.4%) exists, it ought be observed in the neighborhood of these alloys, and such an alloy as H4 ought to show at

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least a nearly homogeneous structure. Therefore, the existence of such a ternary compound as that given by Fuss is very doubtful. We may rather say that X is not $Al₆Fe₂Si₃$.

To ascertain the formula of the unknown compound X , therefore, we prepared many specimens with compositions corresponding to assumed compounds, and examined their microstructures after heat treatment. At last we arrived at the alloy whose microstructure is shown in Photo. 16. As can be seen in this figure, this alloy is an aggregation of needle-like crystals, and we find hardly any other phases. Its composition was found by chemical analysis to be Fe 45.92% and Si 24.57% . As this alloy has the approximate composition of $FeAl₃·FeSi₂$, we may say that the compound X, unknown hitherto, has the fomula $FeAl₃·FeSi₂$.

EQUILIBRIUM DIAGRAM.

Fig. 20 is the general equilibrium diagram obtained from these results. In this figure the regions of the primary separation of (Al), FeAl₃, FeAl₃ FeSi₂ and Si are respectively represented by AEPB, CBPOR, SOPED, and DEF.

BP, PE, OP and DE indicate the uni-variant reaction lines showing respectively

> Liquid \Rightarrow (Al) + FeAl₃, Liquid \preceq (Al) + FeAl₃.FeSi₂, Liquid + $FeAl₃ \nightharpoonup FeAl₃ \cdot FeSi₂$, and Liquid \Rightarrow FeAl_s·FeSi₂ + Si.

In this dagram we denote the invariant points already explained as O , P , and E , and they are summarized in the following table.

Invariant point		Composition %		Temperature \sim	Reaction
	Al	Fe	Si		
Р	Q2		7	615	Liq. + FeAl ₃ \rightleftarrows FeAl ₃ . FeSi ₉ + (Al)
Е	88.4		11.6	578	Liq. \pm (Al)+Si
O	66	23	21	870	Liq. $+ \chi$ \rightleftarrows FeAl ₃ + FeAl ₃ FeSi ₂

Table 3.

CONCLUSION.

We obtained the equilibrium diagram of Al-rich Al-Fe-Si alloys containing up to 30% of Si and up to 32% of Fe. The existence of three invariant reactions was ascertained.

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It was brought to light that the compound *X* of which there has hitherto been no accurate knowledge, is a compound having the compasition $FeAl₃$. FeSi₂ (or Fe₂Al₃Si₂).

ACKNOWLEGEMENT.

In conclusion the writer would like to express his cordial thanks to Prof. Saito by whose aid the present investigation was carried out, and to Mr. Yamagishi who gave a great deal of assistance in this research.