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著者	OGAWA Shiro, MATSUZAKI Yoshinobu
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Study on the Superlattices of Ternary Alloys by X-Ray*

Shiro OGAWA and Yoshinobu MATSUZAKI

The Research Institute for Iron, Steel and Other Metals

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Synopsis

Studies on the superlattices of ternary alloys were recently developed, but only a rew experimental results by X-ray have been reported. The ternary system of iron-aluminum-silicon, which contains the industrially important ferromagnetic alloy "Seudust" and has two superlattices of the same type on the iron-aluminum and iron-silicon sides, offers various interesting problems in connection with the superlattice theory.

The present work was undertaken in this ternary system to confirm by X-ray a composition-range in which the superlattice of the 3 : 1 type can exist, because no work had yet been reported concerning it. The result showed that all ferromagnetic singularities were found in this composition-range.

I. Introduction

Detailed researches have been made in the superlattices of binary alloys and many theories were proposed.(1) The studies on those of ternary alloys, too, have recently been developed. However, in the field of the experimental researches, especially, of the direct ones for the atomic arrangement by X ray, no reports have yet been issued, except for a few on the Heusler Alloy(2) and Fe-Al-Si(3) alloys.

Dr. Yamamoto(4) concluded the existence of the supperlattices of ternary alloys from his detailed study on the influence of heat-treatment on the properties of Fe-Al-Si alloys, such as susceptibility, electric conductivity, etc. A very clear proof by X-ray, however, was not obtained in his study. In the other studies similar to the above, it is also difficult to find any marked report on the experimental results by X-ray, except for Selisky's very short report.(3) Our special attention was, therefore, paid to the importance of the X-ray study on the Fe-Al-Si system, which contains the industrially important ferromagnetic alloy, "Sundust".

Since the atomic arrangement can be directly confirmed by X-ray, it is a very interesting problem whether the atomic arrangement in the superlattices of ternary alloys is of ternary or binary type. Although this point was already confirmed in the Heusler Alloy, it cannot be decided with ease in the case of the Fe-Al-Si alloy system, because the atomic numbers of both alminum and silicon

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* The 618 th report of the Research Institute for Iron, Steel and Other Metals.
A Japanese report of this paper will be published in J. Jap. Inst. Metals, B 15 (1951), No 6, 8.

(1) See, for example, F. C. Nix and W. Shockley, Rev. Mod. Phys., 10 (1938), 1.

(2) V. O. Heusler, Ann. d. Phys., 19 (1934), 155. A. J. Bradley, Proc. Roy. Soc., A., 144 (1934), 340.

(3) I. P. Selissky, J. Phys., USSR., 4 (1941), 567, Jap. Inst. Metals, 5 (1941), 649.

(4) T. Yamamoto, J. Inst. Elec. Eng. Japan, 5 (1947), 175.

are too close to each other to make an appreciable difference between their X-ray scattering factors. The alloys in this system which have the superlattices of the 3:1 type on Fe-Al and Fe-Si sides, Curie temperatures being different from each other, offer various interesting problems, such as (1) the comparison between the theory and the experiment as to the rise of Curie temperature, when silicon is added into the Fe-Al system, (2) the comparison of the ordering degree vs. the temperature curve between the binary and the ternary alloys, (3) the equilibrium-diagramatic research in the stabilization-range in which the superlattices of the 3:1 type and the 1:1 type can exist, etc. In view of the fact that no experimental report on the existence-range of the supperlattices of the Fe-Al-Si system had been issued, we thought it the most urgent problem to bring light on this subject. Therefore, in this paper, the existence-range of the supperlattices of the 3:1 type on the iron-rich side in the Fe-Al-Si system, confirmed by X-ray, will be reported.

II. Experiments

All the specimens were made by the following processes: after being melted in Tammann furnace, they were cast in metallic moulds into sticks, 6 mm in diameter. The central parts taken from the sticks were annealed for 5-6 hours at 900° and then ground into fine powders of 300 mesh. After reheating at 900° to remove strains, they were cooled slowly with the rate of about 30°/hr in the range 800-500°.

Since it is known, in the ternary alloys of Fe-Al-Si system, that the electric resistance at the composition on the line combining Fe_3Al, and Fe_3Si becomes very small,[5] the existence of a superlattice on the above line can be imagined in the first place. Debye photographs of the specimens with the composition at the vicinity of the above-mentioned line were taken with Fe-K_α radiation, and we found the superlattice lines (111), (200), (311), (222) of the Fe_3Al (Fe_3Si) type.[6] (Pl. I and II)* The crystal structure of the Fe_3Al (Fe_3Si) is as shown in Fig. 1. The intensities of the superlattice lines shown in those photographs are nearly unchanged. From this fact it may be said that the positions of Al (Si) in the Fe_3Al (Fe_3Si) lattice are gradually replaced with Si (Al) according to its

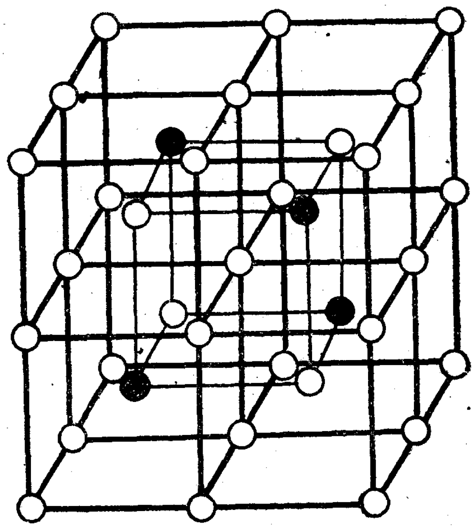


Fig. 1

○ Fe

● Al(Si)

(5) H. Masumoto and T. Yamamoto, Jap. Inst. Metals, 1 (1937), 127.

* (111) and (311) are the characteristic superlattice lines for the Fe_3Al type, and (200) and (222) exist also in the FeAl type.

(6) A. J. Bradley and A. H. Jay, Proc. Roy. Soc. A., 136 (1932), 210. G. Phragmen, J. Iron audSteel Inst. 114 (1926), 397.

quantity. Further experiments were conducted on the basis of the equlibrium diagram by Osawa and Murata of the Fe-Al,(7) Fe-Si(8) systems, in order to find this existence-range. Concerning the equlibrium diagram of Fe-Al system, it is to be added that the next phase following Fe_3Al is FeAl(9) and that the boundary between these two phases was determined by the relation between the intensity of the superlattice lines found by Bradly and Jay(6) and the crystal structure. The results of chemical analysis of the specimens are shown in Table 1, and the experimental results by X-ray in Fig. 2, in which the meanings of the signs are explained. The analytical results of No. 17 and No. 22 are shown in Tables 2 and 3. The comparative numerical values were taken from Osawa and Murata's data.

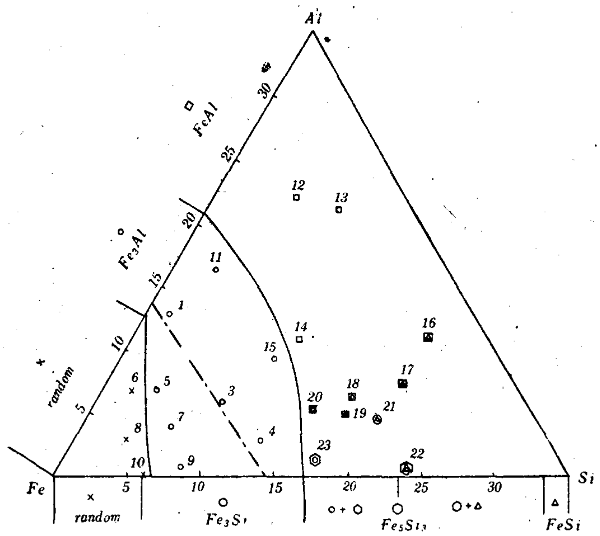


Fig. 2 The composition-range of the superlattice $Fe_3(Al_{1-x}Si_x)$ type in Fe-Al-Si system.

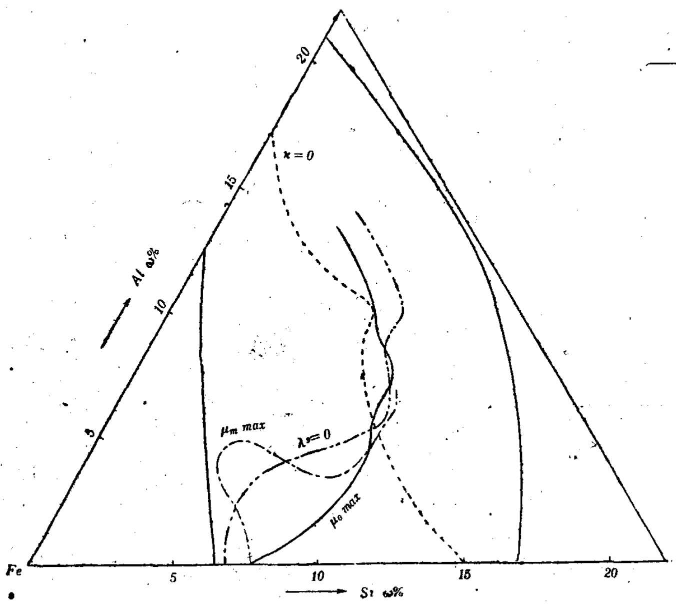


Fig. 3 Relation between the composition-range of $Fe_3(Al_{1-x}Si_x)$ type and the ferromagnetic singularities in Fe-Al-Si system.

Table 1 The results of chemical analysis

No.	Al w%	Si w%
1	12.76	2.65
2	8.59	3.81
3	6.08	8.14
4	2.88	12.21
5	7.21	3.47
6	7.14	1.98
7	4.10	5.50
8	3.20	3.42
9	0.89	8.20
10	0.08	6.33
11	16.70	2.98
12	22.22	5.36
13	21.37	8.63
14	10.89	11.39
15	9.55	9.83
16	11.04	20.04
17	7.35	21.55
18	6.46	16.91
19	5.17	17.49
20	5.70	15.03
21	4.54	20.12
22	0.62	23.71
23	1.47	17.68

(7) A. Osawa and T. Murata, Jap. Inst. Metals, 5 (1941), 259.
(8) A. Osawa and T. Murata, Jap. Inst. Metals, 4 (1940), 229.
(9) H. Sato, Jap. Inst. Metals, 13 (1949), 3.

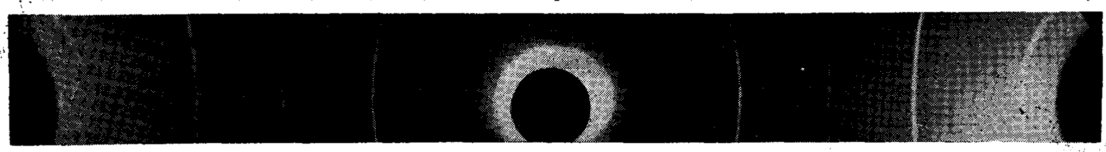
Table 2 The Results of X-ray analysis of No. 17

No. 17			FeSi △			FeAl †□		
No.	I	$1/d^2$ obs.	I	$1/d^2$ obs.	hkl	I	$1/d^2$ obs.	hkl
1	m	0.0965	w	0.0990	110			
2	m	.1170				w	0.1250	100
3	m	.1464	w	.1485	111			
4	m	β .2417	m.w	.2496	210 β			
5	m	.2525				m.w	.2517	110 β
6	v.s	.2450	v.s	.2494	210			
7	v.s	.2492				v.s	.2522	110
8	s	.2844	s	.2996	211			
9	v.w	.3754				v.v.w	.3793	111
10	v.w	β .4980				w	.5083	200 β
11	w							
12	m	.4966				m	.5071	200
13	m	.5439	m	.5509	311			
14	w	β .6909		.7018	321 β			
15	v.w	.5889	v.w	.6005	222			
16	w	β .7491				m.w	.7633	211 β
17	w	.6370		.6504	320			
18	v.s	.6852	v.s	.7002	321			
19	v.s	.7470				v.s	.7614	211
20	v.w	β .9264		.9504	331* β			
21	m	.7832	m	.8000	400			
22	v.w	β .9980		1.049	421* β			
23	m	β 1.012	m.w			w	1.017	220 β
24	v.w	.8468		.8503	410			
25	m	.8871	m	.9002	330			
26	m.s	.9353	s	.9504	331			
27	w	.9823	w	.9995	420			
28	s	.9980				v.s	1.012	220
29	m	1.000	v.s	1.049	421			

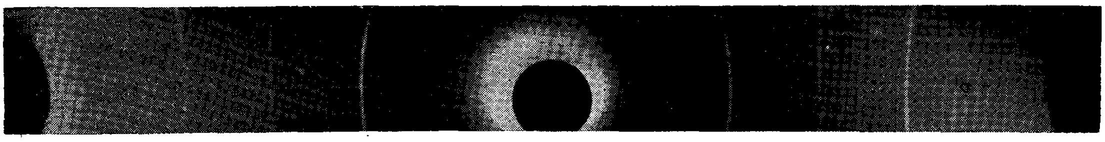
* These lines were not found in Osawa-Murata's table.

† The specimen of FeAl used by Osawa-Murata was silicon-rich and so contained Fe_3Si. After removal of the characteristic lines of Fe_3Si, the indices were divided by two.

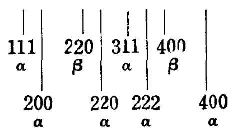
The structures of No. 21 and No. 23 were determined by comparing the results with the photographs of other specimens. Fig. 3 shows the relation between the



Pl. I Specimen No. 2



Pl. II Specimen No. 3



various magnetic properties of the Fe-Al-Si system and the existence-range of the $Fe_3(Al_{1-x}Si_x)$ superlattice. As shown in the figure, the maximum of initial permeability μ_0 and maximum permeability μ_m, magnetostriction constant $\lambda_s=0$ and anisotropy constant $K=0$ are found in this existence-range of the 3:1 type superlattice which we have observed.

Table 3 The Results of X-ray analysis of No. 22

No. 22			Fe_5Si_3 ⬯			FeSi △			Fe_3Si ○		
No.	I	$1/d^2$ obs.	I	$1/d^2$ obs.	hkl	I	$1/d^2$ obs.	hkl	I	$1/d^2$ obs.	hkl
1	v.w	0.0918				w	0.0990	110	w	0.0937	111
2	m.w	.1181	w	0 1180	200				w	.1250	200
3	v.w	.1340	v.w	.1337	112						
4	v.w	.1493				w	.1485				
5	m.w	β .2058	w	.2110	104β	w	.1998	111			
6	m.w	.1810	m	.1812	004			200			
7	v.s	β 2.505 .2057	s m.s	.2525 .2101	212β 104	m.w	.2496	210β	m.w	.2517	220β
8	m.w	β .2690	m.w	.2706	114β						
9	v.v.s	.2495	v.v.s	.2512	212	v.s	.2494	210	s	.2522	220
10	v.s	.2715	s v.s	.2649 .2699	300 114						
11	w	.2931	w	.2993	204	s	.2996	211			
12	w	.3489	v.w	.3542	220				w	.3476	311
13	w	.3764	w	.3834	310				v.w	.3797	222
14	w	.3960	m.w	.4003	205						
15	v.w	β .5001							w	.5083	400β
16	v.v.w	.4282	v.w	.4299	312						
17	v.w	β .5351	v.v.w	.5365	224β						
18	m.w	.4678	w	.4721	400				s	.5071	400
19	s	.5065									
20	s	β .6482 .5320	m.s	.6523 .5365	404β 224						
21	v.w	.5570	v.w	.5650	314	m	.5509	311			
22	w	.6019	m.w	.6054	322						
23	v.s	.6084	v.s m	.6133 .6197	216 410						
24	s	.6577	s	.6518	404						
25	w	β .8447 .7038	w	.8400	503β	v.s	.7002	321			
26	m.s	.7256	m.s	.7227	008						
27	m	.7406	m	.7363	500						
28	v.s	.7600	m.s	.7590	226				v.s	.7614	422
29	v.w	.7901	v.v.w	.7871	316	m	.8000	400			
30	v.w	β .9686	v.v.w v.v.w	.8750 .9888	334β 308β						
31	m.s	.8265	m.s	.8255	420						
32	s	.8325	s	.8384	503						
33	v.v.w	.8604	v.v.w	.9088	:27						
34	v.s	.9088	v.s	.9144	009 510						
35	s	.9210	s	.9276	423 218						
36	m	.9498	m.w	.9565	512	s	.9504	331			
37	m.w	.9592	m.w	.9641	326						
38	m.s	.9686	m.s	.9750	334						
39	s	.9803	s	.9870	308						
40	v.s	1.004				v.s	1.049	421	v.s	1.012	440

In conclusion, as to the melting and casting of the specimens used in this experiments, the authors wish to express their cordial thanks to Prof. Dr. Masumoto, the Director of the Research Institute for Iron, Steel and Other Metals, Tohoku University, for his kindness, and also to Mr. Sugai, member of the same laboratory, for his help. Thanks are also due to Dr. Yamamoto, Professor of the Chiba Technical College, for his suggestive instructions.

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