A Supplement to Investigation of Equilibrium Diagram of Fe-As-C System

(On Magnetic Transformation Point of Fe-As and Fe-As-C System)

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Introduction

The present investigation was carried out for the purpose of determining the magnetic transformation temperature of Fe–As and Fe–As–C alloys and to supplement the previous paper[1]: "The Equilibrium Diagram of Fe–As–C System".

Among magnetic transformations of iron and steel, there is, as the A_0 transformation, the magnetic transformation of cementite at 210°C and, as the A_2 transformation, that of ferrite at 768°C; and also it is known that, in the case of steel containing approximately 0.55 to 0.85 per cent carbon, ferromagnetic ferrite transforms along A_3–line into paramagnetic austenite. In the case of hypereutectoid steel, ferromagnetic ferrite transforms into paramagnetic austenite by A_1 transformation at 723°C.

There are some experimental data reported by P. Oberhoffer and A. Gallaschik[2] concerning the change of magnetic transformation in iron containing arsenic. Their measurement, however, concerned only with the Fe-As binary alloys containing less than 2. 1 per cent arsenic. According to their report, when arsenic is added to pure iron and then heated, the magnetic transformation temperature of this iron is constant at 768°C, but on the contrary, when it is cooled, the magnetic transformation temperature falls, even if the cooling velocity is made extremely

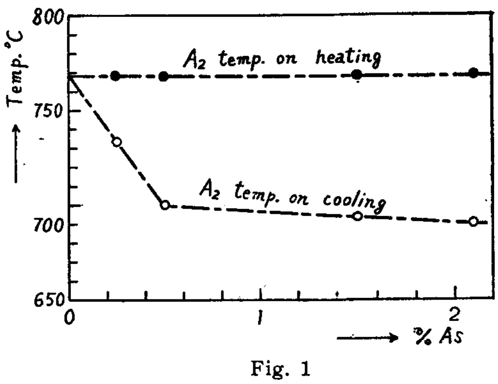

Fig. 1
(P. Oberhoffer and A. Gallaschik)

small. The temperature difference of the magnetic transformation points between heating and cooling, as shown in Fig. 1, is approximately 60°C in the case arsenic is 0.5 per cent and more than 70°C when arsenic is 2.1 per cent.

Preparation of Specimens

Armco iron, Swedish carbon steel, Kenjiho white pig and metallic arsenic, as raw materials, were put into an alundum-lined graphite crucible and were melted in a Tammann or cryptol furnace. 100 or 150 gr was melted at each operation and the molten metal was cast into a cast iron mould or dry sand mould. From the ingots thus obtained, small specimens, 5 mm in diameter and 50 mm long, were made. Their chemical compositions are shown in Table 1. Of these specimens, those annealed before the magnetic analysis were mostly used, however, some of them in their "as cast" conditions-which materials are shown in the note in Table 1-were also used.

Experimental Method and Results

The Honda's magnetometer[3] was used for this magnetic analysis. The experimental process applied was as follows:

A silica tube containing a specimen was inserted into a non-inductive furnace wound by a platinum heating wire. The hot junction of a *Pt-Pt·Rh* thermocouple was contacted at one end of the specimen. After the tube was evacuated, dry nitrogen gas was filled into it until the pressure of the gas became about 1 atmosphere. The heating and cooling rate was 5~10°C/min under 600°C, and $\frac{1}{2}$~1°C/min

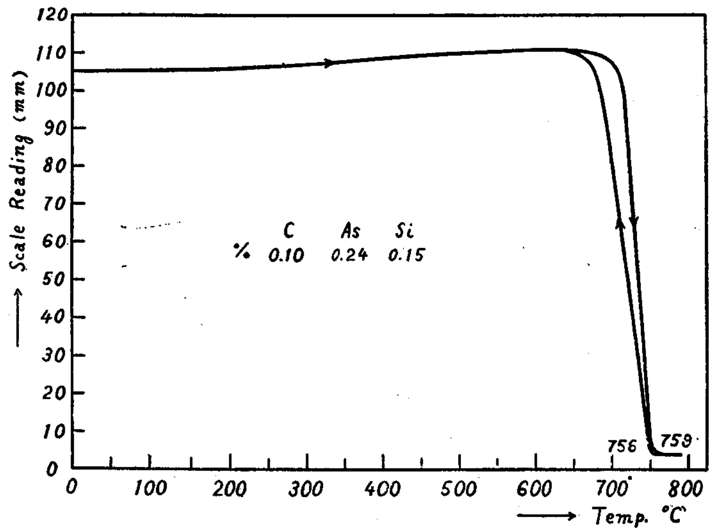

Fig. 2

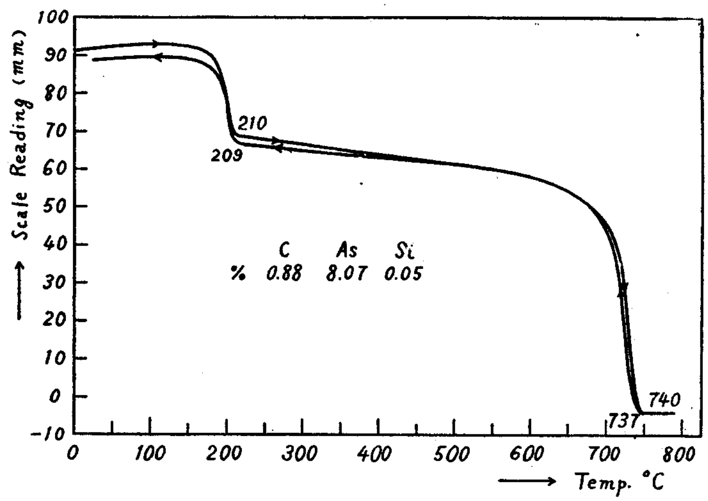

Fig. 3

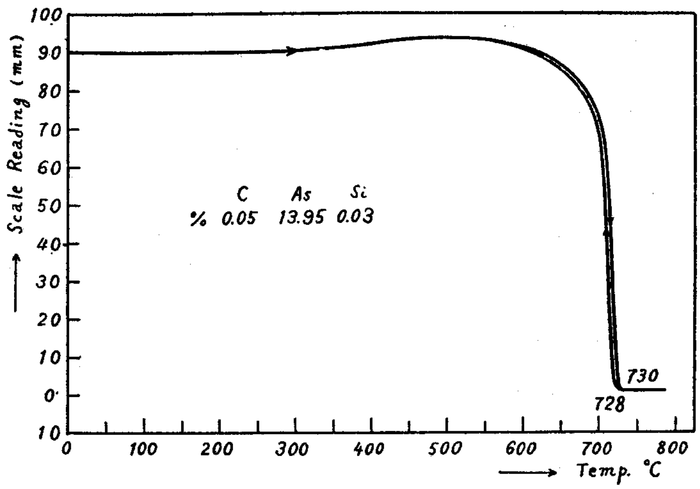

Fig. 4

in the range from 600 to 790°C. The latter heating and cooling rates were employed throughout the range from room temperature to the maximum heating temperature for measuring the magnetic transformation of cementite. Field intensity of our magnetometer was 180 gauss.

Some examples of the curves obtained by these magnetic analyses are shown in Figs. 2, 3 and 4. Magnetic transformation temperatures thus obtained by these curves of temperature versus scale reading are listed in Table 1. These transformation points are plotted in Figs. 5~10 in the corresponding sectional diagrams which were determined in the previous investigation.[1]

Table 1

Specimen		Composition (%)			Transformation temp. °C			Section	Note
No.	Symbol	C	As	Si	Tr. pt.	Heating	Cooling		
1	0.02.0b	0.08	1.99	0.04	A_2	771	770	Fe-As	
2	0.04.0	0.07	4.11	0.04	"	766	766		as cast
3	0.06.0	0.04	5.76	0.05	"	762	757		
4	0.08.0b	0.03	8.28	0.05	"	750	749		
5	0.09.0	0.04	9.69	0.04	"	739	736		as cast
6	0.010b	0.02	10.03	0.04	"	727	725		
7	0.012b	0.02	12.16	0.04	"	732	730		
8	0.013	0.05	13.95	0.03	"	730	728		as cast
11	0.10.3	0.10	0.24	0.15	A_2	759	756	0.25 % As	
12	0.30.3	0.40	0.24	0.72	"	760	758		
13	0.50.3	0.47	0.27	0.61	"	760	757		
14	0.90.3	0.86	0.26	0.47	A_1	760	749		
15	1.10.3	1.00	0.26	0.47	"	757	720		
21	0.00.6	0.05	0.52	0.07	A_2	772	764	0.5 % As	
22	0.30.6	0.48	0.52	1.07	"	760	753		
23	0.70.6	0.67	0.50	0.82	"	769	759		
24	0.90.6	0.83	0.51	0.54	A_1	762	720		
25	1.10.6	1.04	0.54	0.56	"	759	721		
31	0.02.5c	0.05	2.65	0.10	A_2	769	768	2.5 % As	
32	0.32.5	0.22	2.29	0.10	"	771	769		as cast
33	0.52.5	0.47	2.65	0.15	"	769	768		
34	0.72.5	0.61	2.45	0.11	"	761	759		
35	0.92.5	1.01	2.46	0.03	A_1	769	766		
36	1.12.5	1.06	2.62	0.11	"	764	760		
37	1.32.5	1.36	2.60	0.08	" A_0	770 210	766 210		
38	2.02.5	1.90	2.70	0.11	A_1	770	769		
41	0.27.5	0.13	7.54	0.05	A_2	756	749	7.5~8 % As	
42	0.07.5	0.19	7.73	0.05	"	742	740		
43	0.57.5	0.44	7.58	0.05	"	757	749		
44	0.97.5	0.88	8.07	0.05	" A_0	740 210	737 209		
51	0.311	0.20	11.09	0.04	A_2	732	730		as cast
52	0.911	0.74	11.38	0.05	"	730	729		"
53	1.211	1.05	11.30	0.06	"	729	728		"
61	3 c	~0.03	40.4	~0.03	paramagnetic				as cast
62	10 J	"	54.9	"	"				"

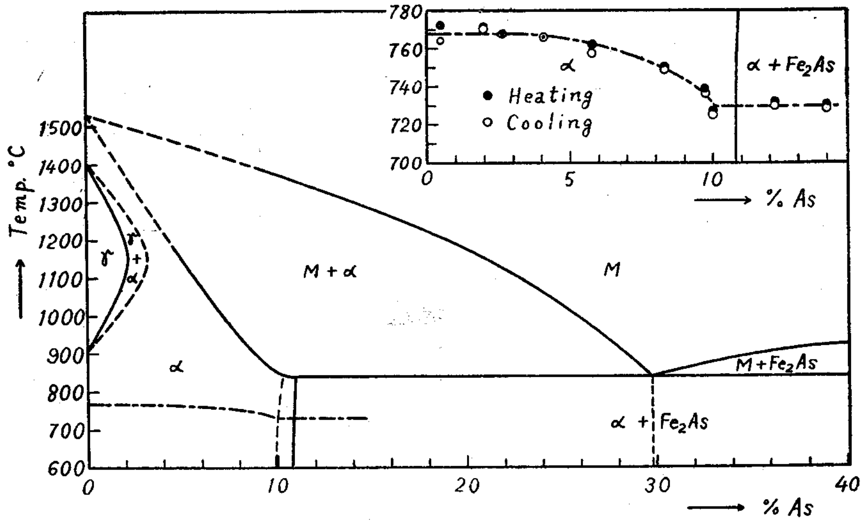

Fig. 5 Fe-As

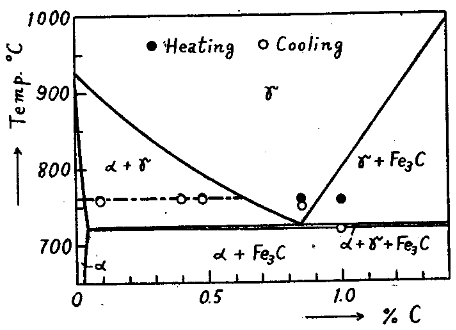

Fig. 6 (0.25% As)

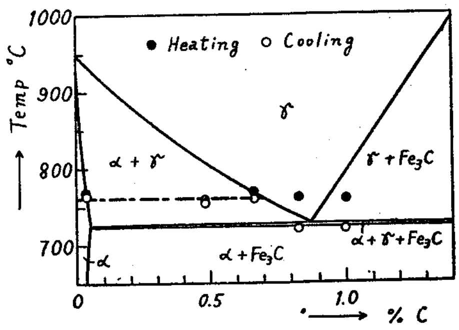

Fig. 7 (0.5% As)

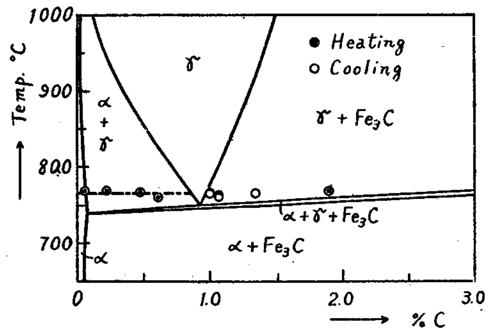

Fig. 8 (2.5% As)

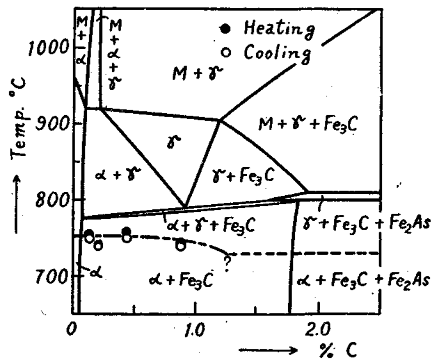

Fig. 9 (7.5～8% As)

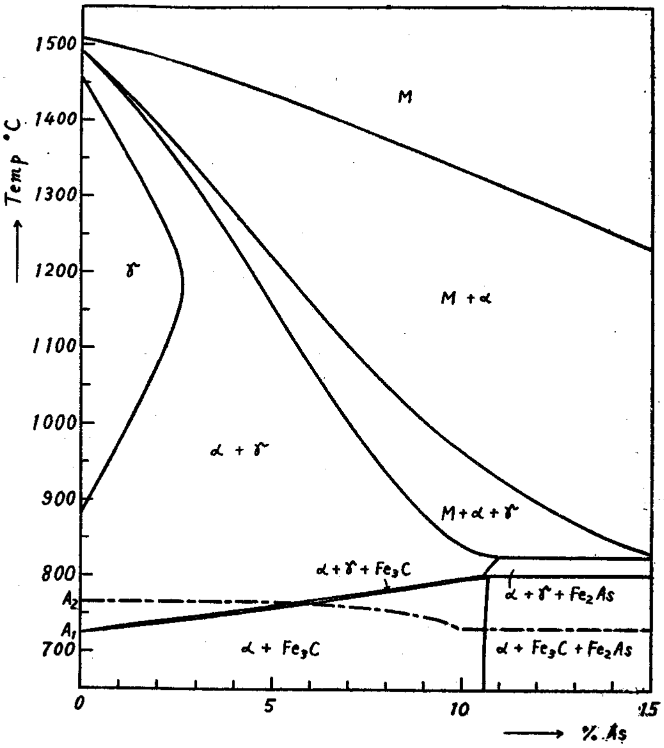

Fig. 10 (0.14% C)

Consideration

In Fe–As binary alloys containing less than 4 per cent arsenic, the magnetic transformation temperature A_2 is constant at 768°C and it falls gradually as the content of arsenic in the alloy increases, then it becomes constant at 730°C when the content of arsenic becomes more than 10 per cent. From this result, the solubility limit of arsenic in ferrite is conceivable to be about 10 per cent at 730°C which is a little less than the solubility value (11 per cent) in our previous investigation.

We consider that the value obtained by the present experiments is more accurate than that obtained previously (11 per cent) which was determined mainly by examining the microscopic structure of the annealed specimens. It is certain, however, that the solubility limit of arsenic in ferrite is higher than the value (ca. 7 per cent) obtained by Oberhoffer and Gallaschik.[2] Remarkable temperature differences of the magnetic transformation points between heating and cooling reported by them were not observed in this experiments.

Both the Fe–As binary alloy containing 40.4 per cent arsenic (No. 61), i. e. the specimen nearly composed of pure Fe_2As (40.16 per cent arsenic), and the binary alloy containing 54.9 per cent arsenic (No. 62), i. e. the specimen consisting in two phases of Fe_2As and FeAs were set into the measuring apparatus but in either case the deflection of scale reading did not occur. Next, both of these specimen were pulverized and when they were drawn close to a permanent magnet, a part of them was attracted to the edge of the magnet. Therefore, the compound Fe_2As is a paramagnetic substance and FeAs appears most likely paramagnetic.

The A_2 transformation temperature of Fe-As-C ternary alloys falls gradually as their content of arsenic increases as shown in Figs. 6~9, and becomes constant at 730°C in the range of composition of the alloy where two phases- ferrite and Fe_2As- or three phases-ferrite, Fe_2As and cementite- are in equilibrium. Eutectoid point A_1 (0.85 per cent carbon) at 723°C in the Fe-C binary alloy changes its position gradually to higher temperature range as the content of arsenic in steel increases, and it reaches a peritecto-eutectoid point (0.9 per cent carbon and 9.0 per cent arsenic) at 800°C.[1]

In Fe-As-C ternary alloys, therefore, the temperature of A_2 point is higher than that of A_1 when the content of arsenic in the alloy is low, then these two temperatures become equivalent, and as the content of arsenic increases more, the temperature of A_2 becomes lower than that of A_1. The intersecting point lies in the vicinity of a straight line horizontally connecting the point of Fe-As binary system with 6 per cent arsenic content at 762°C and the point of Fe-As-C ternary system on the cementite axis at the same temperature. The relative relation of the temperature change of A_1 and A_2 points is shown in the sectional diagram for 0.14 per cent carbon (Fig. 10).

Several specimens were tested to find out about the A_0 transformation point of cementite, but it was difficult to detect the A_0 transformation temperature of the low carbon specimen because of little change in scale reading. However, in the case of specimens No. 37 (1.36 per cent carbon and 2.60 per cent arsenic) and No. 44 (0.88 per cent carbon and 8.07 per cent arsenic), the A_0 transformation was clearly observed as shown in Fig. 4. Its temperature is constant at 210°C regardless of the content of arsenic in steel, which is the same as in the case of the Fe-C binary alloy. Consequently, it is assumed that the solubility of arsenic in cementite is close to zero.

Among the specimens used were some containing a considerable amount of silicon, however, the existence of silicon seemed to have no effect at all on magnetic transformation. Neither was the difference recognized of its influence upon magnetic transformation between the annealed specimen and the as-cast specimen.

Summary

The magnetic analyses of thirty-five kinds of iron and steel containing arsenic were performed and their A_2, A_1 and A_0 transformation temperatures were measured.

The results obtained are as follows:

(1) A_2 transformation temperature of Fe-As binary alloys is constant at 768°C when the arsenic content is less than 4 per cent, then it falls as the content of arsenic increases and it again becomes constant at 730°C in the alloys containing more than 10 per cent arsenic.

(2) The solubility limit of arsenic in ferrite of Fe-As system is about 10 per cent at 730°C.

(3) Fe_2As is a paramagnetic substance and FeAs also appears to be paramagnetic.

(4) In Fe-As-C ternary alloys, the transformation temperature at A_2 point falls gradually as their content of arsenic increases, and in the range of composition of the alloys where two phases- ferrite and Fe_2As- or three phases- ferrite, Fe_2As and cementite- are in equilibrium, the A_2 transformation temperature becomes constant at 730°C.

(5) In Fe-As-C ternary system, the temperature of A_2 transformation point becomes lower than that of A_1 transformation point as the content of arsenic becomes greater.

(6) Arsenic contained in steels has no effect on their A_0 transformation temperature within the range examined in this investigation.

Acknowledgment

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References

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3) K. Honda; Science Report of the Tohoku Imperial University, **5** (1916) 285.