On the Order-Disorder Transformation of the Alloys of Iron and Cobalt*

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Synopsis

The specific heat of 17 alloys in the range of α solid solution of iron and cobalt system has been measured. It has been found that there are 3 maximum portions on the curve of temperature of the maximum of specific heat against concentration, besides one corresponding to the transformation of FeCo superstructure; the 3 portions extend over the concentration ranges of 20 to 29, 34.6 to 66 and 66 to 78 per cent of cobalt, respectively. The maximum portion in the range of 34.6 to 66 per cent of cobalt has been already found by S. Kaya and H. Sato and is considered by the present investigators to be due to a lattice transformation of FeCo superstructure. The other maximum portions, in the ranges of 20 to 29 and 66 to 78 per cent of cobalt, are considered to be due to the existence of superstructures of Fe_3Co and $FeCo_3$, respectively.

I. Introduction

In 1925, one of the present investigators(1) discovered the existence of the allotropic transformation of cobalt for the first time. Then, he made a further inquiry into the alloys of iron and cobalt and found that in the α solid solution range of the alloy system there exists conspicuous anomalies unobservable in an ordinary solid solution. As an example the relationship between the electric conductivity and the cobalt concentration is shown in Fig. 1. As can be seen in this figure there are 3 maxima on the curve at the concentrations of about 27 per cent, about 51 per cent and about 75 per cent of cobalt, respectively. However, as the existence of superstructure had not been found at that time, the above-mentioned anomalies remained to be explained.

Later, in 1941, C. Ellis and E.S. Greiner(2) discovered the existence of the superstructure FeCo by the use of X-ray and thermal analysis; and in 1943, Drs. S. Kaya and

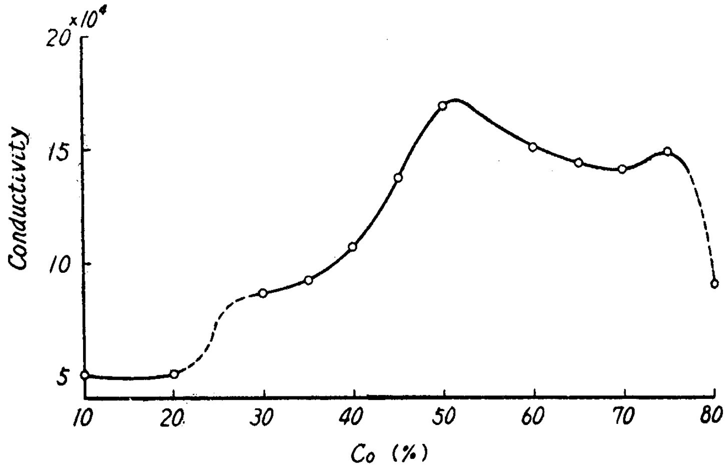

Fig. 1. Electric conductivity of Fe–Co alloys measured by H. Masumoto in 1925.

* The 772nd report of the Research Institute for Iron, Steel and Other Metals. Read at the autumn meeting of the Japan Institute of Metals, Oct. 10, 1951. Published in the Nippon Kinzoku Gakkai-Si (J. Japan Inst. Metals), **17** (1953), 312.

(1) H. Masumoto, Kinzoku no Kenkyû, **2** (1925), 877, 1023; Sci. Rep., Tôhoku Imp. Univ., **15** (1941), 45.

(2) C. Ellis, E. S. Greiner, Trans. Amer. Soc. Metals, **29** (1941), 45.

H. Sato[3] made a detailed study of this superstructure. In the same year the present investigators independently carried out a preliminary experiment on the specific heat with some alloys of this system and, comparing the results obtained with those by one of the present investigators mentioned above, anticipated the existence of the superstructures, Fe_3Co and $FeCo_3$. But the war had prevented a further study of them. Recently, however, they have measured the specific heat of the alloys in the whole α phase of iron and cobalt system, the results of which will be described in the followings.

II. Specimens and method of measurement

The materials used for preparing the alloys are electrolytic iron and elctrolytic cobalt. The results of the chemical analysis of the metals used are shown in Table 1.

Table 1. Results of chemical analysis of metals used.

Metal	Fe(%)	Ni(%)	C (%)	Si(%)	Mn(%)	Al(%)	P (%)	S(%)
Electrolytic Co	0.16	0.31	0.031	0.006	0.003	Trace	0.001	Trace
Electrolytic Fe	—	—	0.04	0.021	0.005	0.02	0.002	None

The above-mentioned materials were first melted in a hydrogen atmosphere with a Tammann furnace and slowly cooled in a crucible; after forging the solidified alloy slightly, it was lathed into a cylinder 18 mm in diameter and 38 mm in length. Finally an aperture 3 mm in diameter and 17 mm in depth was drilled into the cylinder from both bases along its central axis. The cylinders thus finished were used as specimens. The cobalt content of the specimens is shown in Table 2. For the measurement in an annealed state, the specimens were all annealed in a vacuum furnace at 1000° for 2 hours and thereafter cooled down to 420° at a rate of 30° per hour. Then, after they were held at that temperature for 10 days, they were further cooled down to room temperature at the same rate.

Table 2. Temperatures of the maxima on the specific heat curves of the alloys of iron and cobalt.

Co(%)	a FeCo	b Fe_3Co	c (FeCo)	d $FeCo_3$
20		515°		
23		550		
26		565		
29	580°	535		
31	604			
34.6	644		540°	
42	695		565	
47	711		590	
51.4	725		553	
56	703		515	
61	668		480	
66	601		(450)	(450°)
67.3	597		(435)	(435)
70	555			473
73				475
76				455
78				450

The measurement of the specific heat was carried out in vacuum with the apparatus based on an inverse rate curve method which was used previously by the present investigators[4] for the measurement of the specific heat of the copper and zinc alloys.

(3) S. Kaya, H. Sato, Proc. Phys. Math. Soc., Japan, **25** (1943), 261.
(4) H. Masumoto, H. Saitô, M. Sugihara, Nippon Kinzoku Gakkai-Si, **16** (1952), 359; Sci. Rep., RITU., **A4** (1952), 481.

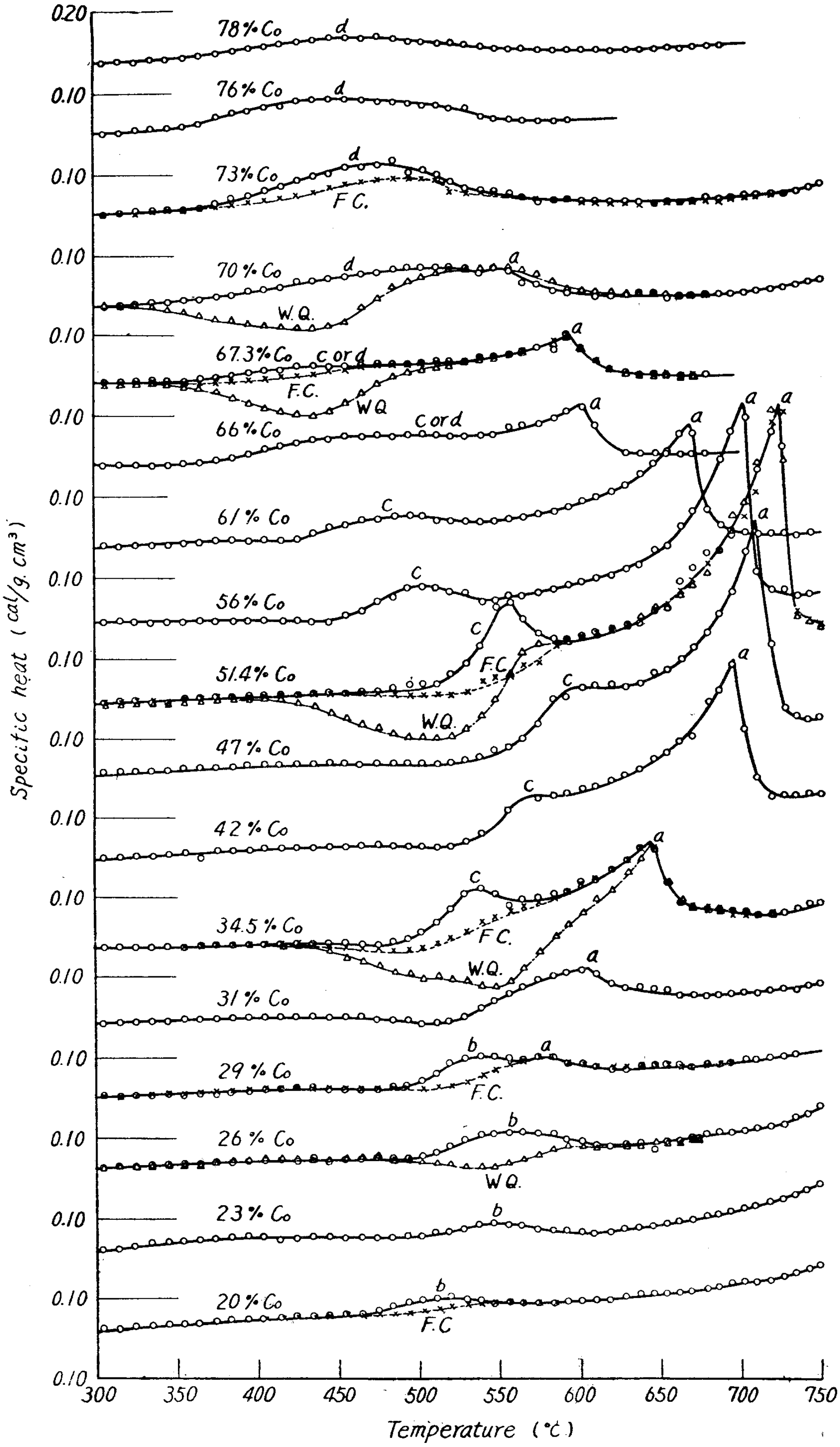

Fig. 2. The specific heat curves of Fe–Co alloys, annealed at 420° for 10 days, cooled rapidly in a furnace and quenched into water from 700°.

III. The results of measurement

The results of measurement of the specific heat of the annealed alloys of iron and cobalt are shown in Fig. 2.

As seen in this figure, a small maximum (b) can be observed at about 515° on the specific heat curve for the alloy containing 20 per cent of cobalt. This maximum shifts to the high temperature side and simultaneously becomes conspicuously large with an increase of cobalt content, reaching the highest temperature of 565° and becoming largest in the alloy containing 26 per cent of cobalt. With a further increase of cobalt content, this maximum shifts again to the low temperature side and simultaneously becomes small, being unobservable in the alloy containing 31 per cent of cobalt. The temperatures of this maximum are collected in the 3rd column of Table 2, and graphically shown in Fig. 3 by the curve (b).

Next, in the case of the alloy containing 29 per cent of cobalt, another small maximum (a) can be observed at about 580° in addition to the above-mentioned one. This maximum gradually shifts to the high temperature side and simultaneously becomes large with the increase of cobalt content, becoming largest and highest of 725° in the alloy containing 51.4 per cent of cobalt. This maximum has also been observed in the measurement by Drs. Kaya and Sato[3], and it is clear that the maximum is due to the transformation of FeCo superstructure. As the quantity of added cobalt is further increased, this maximum shifts to the low temperature side and gradually becomes small, being barely observable in the alloy containing 70 per cent of cobalt. The relations between the temperatures of the said maximum and the cobalt contents are given in the 2nd column of Table 2 and graphically shown in Fig. 3 by the curve (a). In Fig. 3, the result by Ellis and Greiner, and that by Kaya and Sato are shown as well by way of comparison.

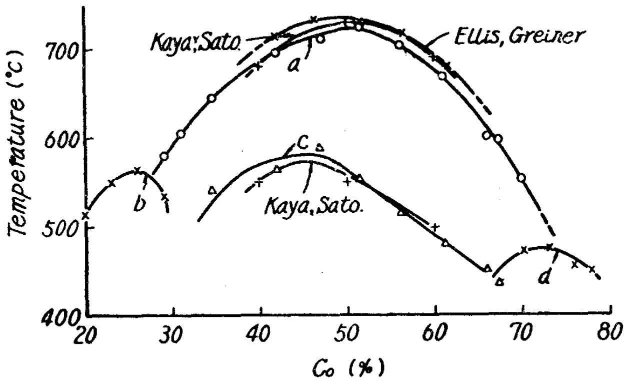

Fig. 3, The temperatures of the maxima on the specific heat curves of Fe-Co alloys.

As seen in Fig. 2, no other anomaly can be observed than the one (a) due to the transformation of FeCo in the alloy containing 31 per cent of cobalt, but when the cobalt content increases to 34.5 per cent, another maximum (c) shows itself. The latter maximum also shifts gradually to the high temperature side and simultaneously becomes conspicuously large, as the quantity of added cobalt is further increased, till the highest temperature 590° is reached in the alloy containing 47 per cent of cobalt; it is however in the alloy containing 51.4 per cent of cobalt that this maximum becomes largest. When the quantity of added cobalt is further increased, the maximum shits to the low temperature side almost linearly and similtaneously becomes small; but the limit of the existence of this maximum is not clear. That is to say, although in the alloy containing 67.3 per cent of cobalt a maximum exists in the neighbourhood of 435° covering an extensive range, it cannot be concluded merely from the results by the present investigation whether, this one corresponds to the maximum (c) or to the maximum (d) which is to be described in the next paragraph. The relations between the temperatures of the maximum (c) and the cobalt contents are given in the 4th column of Table 2, and graphically shown in Fig. 3 by the curve (c). In the figure, the rough temperatures obtained by Drs. Kaya and Sato are also shown, which are almost the same as those obtained by the present investigators.

Further, in the alloy containing 70 per cent of cobalt another maximum (d) exists at about 473° besides the maximum (a) corresponding to FeCo superstructure transformation. This maximum reaches the highest temperature (about 475°) in the alloy containing 73 per cent of cobalt and simultaneously becomes largest; but as the quantity of added cobalt is further increased, it shifts to the low temperature side and simultaneously becomes small. The temperatures of this maximum are given in the 5th column of Table 2, and graphically shown in Fig. 3 by the curve (d).

In Fig. 2 are graphically shown the results of the measurement of the alloys containing respectively, 20, 29, 34.5, 51.4, 67.3, and 73 per cent of cobalt all of them furnace-cooled from 800° to room temperature in about 4 hours (F.C.) and the results of the measurement of the alloys containing respectively 26, 34.5, 67.3, and 70 per cent of cobalt all of them quenched in water from 700° (W.Q.). As seen in this figure, the maximum (a) on the curves F. C. and W. Q. corresponds with that of the annealed alloys, which fact shows that the superstructure FeCo can be completely reproduced by heating at a rate of about 2° per minute irrespective of the previous heat treatment. On the other hand, each of the maxima (b), (c) and (d) is much influenced by heat treatment, becoming small when furnace-cooled, and also a valley when quenched. Of these four maxima, the appearance of the maximum (a) is due, as mentioned above, to the FeCo superstructure, while the maximum (c) seems to be caused by a lattice transformatioe of the FeCo superstructure, the crystal structure of which is, however, still unknown.

In the Fig. 3, the two curves (b) and (c) are separated from each other at the concentration of 31 per cent of cobalt and the curve (c) also seems to be separated from the curve (d), when viewed from the relations between its temperature and the cobalt content. The position of the maximum of these curves nearly corresponds with that of the maximum of the electric conductivity as shown in Fig. 1. Therefore, the present investigators consider that the maxima (b) and (d) in Fig. 2 are due to the transformation of superstructures Fe_3Co and $FeCo_3$ respectively. As for the anomaly in the neighbourhood of $FeCo_3$, Mr. T. Yokoyama[(5)] made a systematic measurement of its hardness changes by heat treatment at the same time

(5) T. Yokoyama, Lecture at the autumn meeting of the Japan Institute of Metals, Oct. 10, 1951.

when the present investigators carried on this experiment, and looks ahead for the probable existence of the superstructure as they do.

Summary

The specific heat of the α phase alloys of the Fe-Co system was measured and the following results were obtained:

(1) The maximum on the specific heat curve, which corresponds to the transformation of the FeCo superstructure, can be observed in the range between 29 per cent and 70 per cent of cobalt, and it is largest in the alloy containing 51.4 per cent of cobalt and its temperature also is highest in the same alloy.

(2) In the range between 34.6 per cent and 67 per cent of cobalt, in addition to the maximum due to FeCo superstructure, can also be observed a small maximum on the specific heat curve, whose temperature is highest in the alloy containing 47 per cent of cobalt and who is largest in the alloy containing 51.4 per cent of cobalt. This seems to be due to a lattice transformation of the FeCo superstructure.

(3) In the range between 20 per cent and 29 per cent of cobalt, a maximum on the specific heat curve can be observed. The maximum is largest and highest in temperature in the alloy containing 26 per cent of cobalt. This maximum is remarkably influenced by heat treatment, and seems to be due to the transformation of the Fe_3Co superstructure.

(4) In the range between 70 per cent and 78 per cent of cobalt, there is a maximum on the specific heat curve who is largest and highest in temperature in the alloy containing 73 per cent of cobalt. This maximum is remarkably influenced by heat treatment, and seems to be due to the transformation of the $FeCo_3$ superstructure.

In conclusion, the present investigators wish to express their deep gratitude to Mr. Yutaka Sugai who cordially gave them much assistance during this experiment.