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Effect of Cooling Rate on A_3 Transformation Temperatures of Iron and Iron-Nickel Binary Alloys*

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Synopsis

Effects of cooling rate on A_3 points of a few pure irons, iron-low carbon alloys and iron-nickel alloys have been examined at cooling rates between 100°C/sec and 60,000°C/sec by using a gas quench apparatus. A_3 point of iron containing less than 0.003 wt% C falls gradually with the increase in cooling rate and continuously approaches a fixed temperature (maximum supercooled A_3), but in the iron containing more than 0.006 wt% C it falls discontinuously to the Ms temperature at the cooling rate of about 20,000°C/sec. Maximum supercooled A_3 points of these irons are affected seriously by a very small content of carbon below 0.005 wt% C, falling remarkably from about 720°C at 0.001 wt% C to about 650°C at 0.003 wt% C with increasing carbon content. In the case of iron-nickel alloys it falls with increasing cooling rate and discontinuously by about 100°C at a certain cooling rate which depends on the nickel content. The drop of the transformation temperature is independent of a further cooling rate. The critical cooling rate decreases from about 25,000°C/sec at 1% Ni to about 2,000°C/sec at 20% Ni. The Ms points of these alloys are in agreement, at higher nickel concentrations, with those reported previously, but are displaced to a lower temperature side at lower nickel concentration.

I. Introduction

It was formerly considered that Fe-Ni binary alloys containing nickel up to about 33 per cent transformed from austenite into martensite at a comparatively low cooling rate (around 10°C/min), irrespective of nickel content. However, it has recently been found(1),(2) that iron-low nickel binary alloys transform at lower temperatures than the Ms points formerly measured, and thus, such Ms points have come to be regarded to correspond to the points initiating transformation based on another mechanism than that of martensite. Also, it is known that, when the Ms point of Fe-Ni binary alloy is expressed as a function of composition and extrapolated to Ni%=0 to obtain Ms point of pure iron, it results in 910°C, largely different from that(3) extrapolated from Fe-C alloy.

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* The **1463rd** report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in the J. Japan Inst. Metals, **34** (1970), 286.

(1) W.D. Swanson and J.G. Parr, J. Iron Steel Inst., **202** (1964), 104.

(2) E.A. Wilson, Ph. D. Thesis, Univ. of Liverpool (1964).

(3) A.B. Greninger, Trans. ASM, **30** (1942), 1.

In the present work, the reexamination of transformation points of iron and iron-low nickel binary alloys and the effect of cooling rate on A_3 points were studied.

II. Experimental method

Table 1 shows chemical compositions of iron used. Specimen A is a pure iron obtained from an iron salt, which was synthesized into a stable organic metal compound and processed with an organic compound refining method(4); specimens B and C are commercial Johnson Matthey pure iron and electrolytic iron, respectively, and D, E and F were obtained after a process that the above electrolytic iron was combined with white pig iron melted in vacuum and was together melted in vacuum in a high-frequency induction furnace. In preparing specimens of Fe-Ni binary alloys, electrolytic iron brought into a size of 0.5 to 1 cm cube was heated to become decarburized in a wet hydrogen atmosphere at 800°C for 8 hr, and then reheated to remove oxides for 8 hr in a dry hydrogen atmosphere with a dew point of about -60°C. As a result, the carbon in the electrolytic iron was reduced to less than 0.002 per cent. This iron was combined with nickel of 99.99 per cent in purity and was together melted in an argon-arc furnace with non-consumable electrode for experimental Fe-Ni binary alloys. The ingot obtained had a form of flat ellipse, about 70 g in weight. Analysis of impurities in the specimen was made only as to carbon and nitrogen, both of which greatly influence the transformation points. The results of the analyses are shown in Table 2.

Table 1. Chemical composition of pure irons and iron-low carbon alloys (wt%)

Specimen	C	Si	Mn	P	S	N
A	0.001	—	—	—	—	0.001
B	0.002	—	—	—	—	0.001
C	0.003	0.008	0.002	0.004	0.005	0.002
D	0.006	0.009	0.001	0.002	0.007	0.002
E	0.018	0.014	0.001	0.002	0.007	0.001
F	0.039	0.019	0.001	0.002	0.007	0.002

The ingot was then hot-forged into a plate, about 2 mm in thickness, and after the scales on the surface were removed, this was cold-rolled into a plate-form specimen, 0.2 mm in thickness. Then, pure iron specimens listed in Table 1 were heated at 1,000°C for 2 hr, and Fe-Ni alloy specimens at 1,200°C for 8 hr, both in vacuum to become homogeneous. Then 0.2 mm-thick plate specimen was carefully scissored out into a new shape, approximately 0.25 mm both in length and width. Thus, the finished specimen is rather small in size, but this is indispensable to obtain cooling rates in a wide range. On the other hand, the specimen is in

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(4) A. Arakawa, Proc. Phys. Soc. Japan, **21** (1966), 523.

Table 2. Chemical composition of iron-nickel alloys (wt%)

Specimen	Ni	C	N
NI-1	1.01	0.002	0.002
NI-2	2.06	0.002	0.002
NI-3	5.16	0.001	0.001
NI-4	10.58	0.002	0.001
NI-5	15.29	0.002	0.002
NI-6	20.47	0.001	0.002

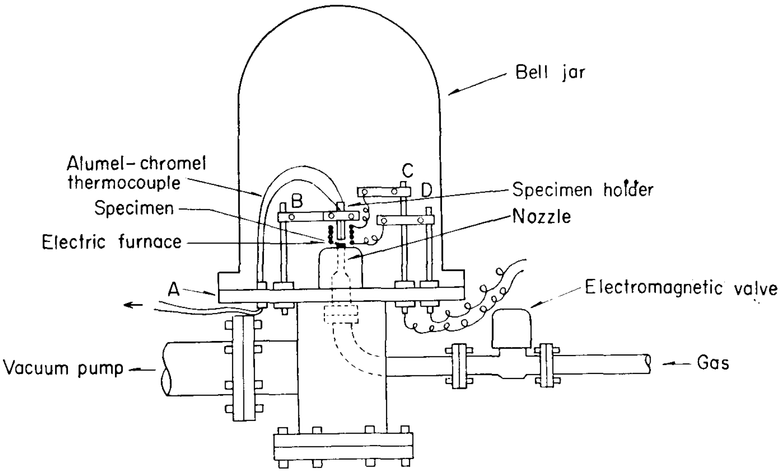

Fig. 1. Gas quench apparatus of Parr's type.

thickness, 2000 to 3000 times as large as that for electron microscopy, and is considered to display properties almost the same as those of a bulk specimen.

For quenching, a gas quench apparatus similar to the one reported by Parr et al.(5) was prepared, which is illustrated in Fig. 1. In the figure A, is a brass flange, about 20 cm in diameter, which is equipped with 3 supporters, marked by B, C, and D, of which C and D are electrodes of copper, and B is made of stainless steel and has at its tip a specimen holder made of porcelain. The specimen is heated by a tungsten wire, 0.5 mm in diameter, and there is a nozzle for cooling just below the specimen. A gas pipe connecting the nozzle is equipped with an electromagnetic valve and its end is connected with a gas bomb. The specimen was spot-welded to a chromelalumel thermocouple, 0.08 mm in diameter, and was set at the edge of the specimen holder. The specimen, electrodes, and nozzle were wholely covered by a bell jar, and the inside of the apparatus was made vacuum up to 1×10^{-4} mm Hg, and then the specimen was heated. Each specimen was austenitized at 1,000°C for 30 sec. The effect of heating time was examined with the specimens of the same composition by varying the time from 10 sec to 5 min, but no difference in the effect was observed. For cooling, argon or hydrogen gas

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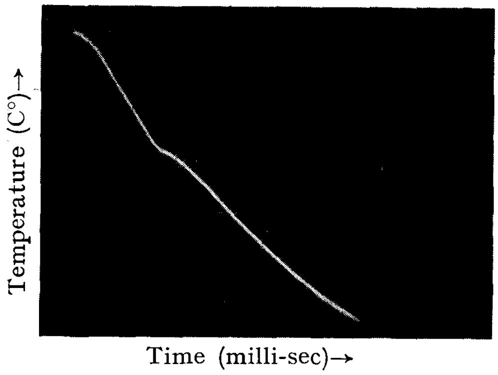
(5) M.J. Bibby and J.G. Parr, J. Iron Steel Inst., **202** (1964), 100.



Phot. 1. Typical cooling curve.

was used, and the cooling rate was adjusted by changing the pressure at the gas outlet of the bomb, by which the rate of cooling was made around 100°～60,000°C/sec. The cooling state of specimens was observed with a synchroscope and photographed. The cooling curve thus obtained indicated at its distinct bend the point of transformation. An example of the curve is shown in Phot. 1.

III. Results and discussion

1. Pure iron and iron-low carbon alloys

Figs. 2～4 show the effects of cooling rate on A_3 points of pure iron and iron-low carbon alloys. As shown in the figures, as the cooling rate increases, the transformation point gradually lowers and reaches a constant temperature. This constant temperature lowers as carbon content increases, and as shown in Fig. 4, over 0.006 wt% C the transformation occurs at two separated levels, apparently like the relation of Ar′ and Ar″ points to cooling rate, But different from Ar′ and Ar″ relation, the transformation points were scarcely observed together on the two levels in a cooling curve, but in one case were measured at upper level and in the other case at lower level and not scattered even if much the same cooling rate was used. This fact is to be marked. In the case of pure iron containing less than 0.003% carbon, the transformation points at two levels were not observed. Parr et al.(5), in quenching pure iron containing 0.0017% carbon, have observed that the transformation points become discontinuous at the cooling rate around

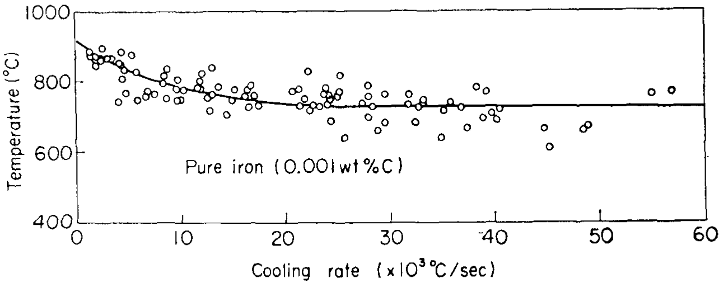


Fig. 2. Effect of cooling rate on A_3 transformation temperature of pure iron.

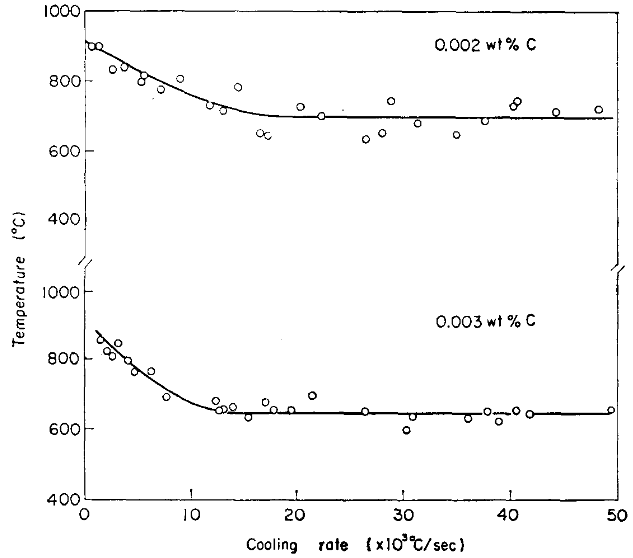


Fig. 3. Effect of cooling rate on A_3 transformation temperature of irons.

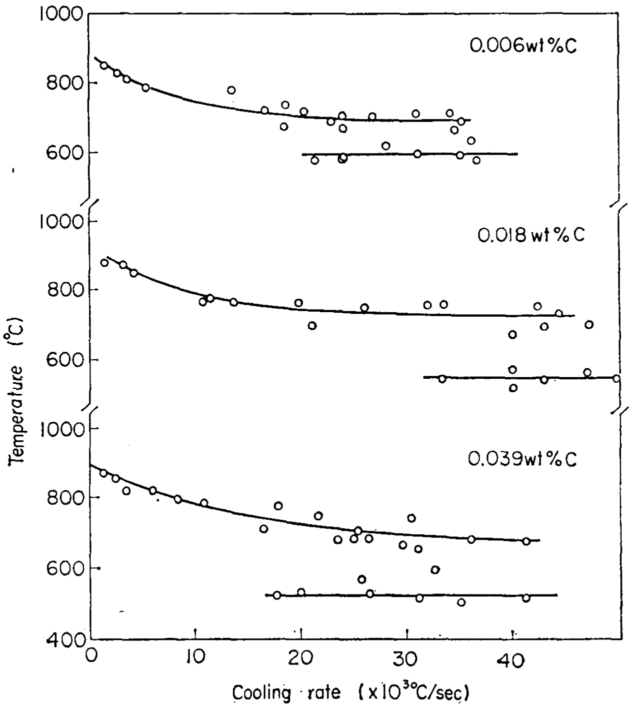


Fig. 4. Effect of cooling rate on A_3 transformation temperature of iron-low carbon binary alloys.

35,000°C/sec, and a certain constant transformation temperature exists, independent of the cooling rate, at around 750°C, about 50°C lower than the supercooled A_3 point. In Fig. 2, experimental values are considerably scattered and no clear sign of discontinuity is discernible, probably due either to the values too scattering to detect such discontinuous points or to the amount of impurities influentially different between the specimens used by Parr et al. and those in the present experiment. So, to coordinate the experimental values, an attempt was made in the following way:

Assuming that the transformation temperature T decreases monotonously from 910°C with the increase in cooling rate V, and that a cooling curve shows no slope at a critical cooling rate V_c, the following differential equation can be formulated:

$$dT/dV = k\,(V_c - V)^n, \tag{1}$$

where k is the proportional constant V_c, is the critical cooling rate, and n is also a constant. Then, with

$$T = 1183°\mathrm{K}, \quad dT/dV < 0, \quad \text{when } V = 0,$$

$$T = T_{ex}, \quad dT/dV = 0, \quad \text{when } V = V_c,$$

Eq. (1) can be solved into the following equation:

$$T = (1183 - T_{ex})\,(1 - V/V_c)^{n+1} + T_{ex}, \tag{2}$$

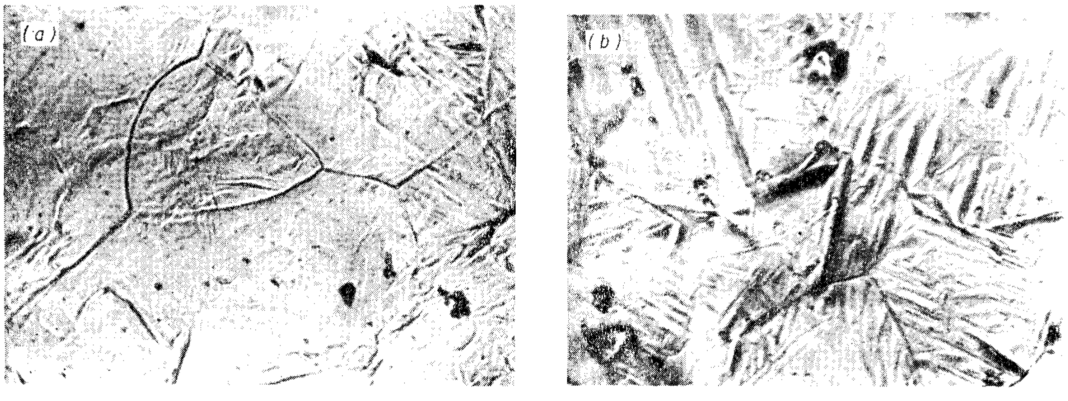
where T_{ex} is the temperature corresponding to $dT/dV=0$. In the above experimental formula unknown values of T_{ex}, V_c, and n can be determined by least square of a non-linear equation by using the values shown in Fig. 2. The result is

$$V_c = 0.1 \times 10^6, \quad T_{ex} = 997°\mathrm{K}, \quad n = 10.7 \tag{3}$$

and thus, Eq. (2) becomes the following:

$$T = 186\left\{1 - V/(0.1 \times 10^6)\right\}^{11.7} + 997 \tag{4}$$

The solid line in Fig. 2 has been drawn according to Eq. (4). According to Eq. (3), the maximum supercooled A_3 point is 723°C, and the supercooled A_3 transformation is to be observable within the range up to the cooling rate of 0.1×10^6 °C/sec. Phot. 2 shows the surface structure of a transformed specimen. As shown by (b) in the photograph, a martensitic surface ruggedness is observable even at the cooling rate of 55,000°C/sec, which structurally agrees with that shown by Parr et al.(5), who concluded this as martensite. In the present work, it has not been determined that this structure is martensite. However, it is to be noted that



Phot. 2. Surface structures of pure iron (0.001%C) polished and quenched from 1000°C at a rate of (a) 20000°C/sec and (b) 55000°C/sec (×900×2/3).

the $\gamma \rightarrow \alpha$ transformation of pure iron, even at a slow cooling at 910°C, partially includes a mechanical shearing(6),(7); a calculation with the data of diffusion(8) clearly shows that the transformation cannot be completed solely by the diffusion mechanism in such a short time as 0.01 sec, and surface ruggedness is observable as shown in Phot. 2(b). When all these are considered together, it is probable that the shearing mechanism also plays a significant role in the transformation.

As already shown in Fig. 4, when carbon content becomes 0.006 wt%, transformation points show a tendency to appear at two levels, which is very evident in the cases of 0.018 wt% C and 0.039 wt% C. Of these, the transformation points at lower temperatures may be considered as Ms points(5),(9),(10). Lower transformation points of Fe-C alloys (0.018 and 0.039 wt% C), when plotted against carbon content as shown in Fig. 6, conform to the extrapolation of the plotting of Ms points. Although no systematical regularity is discernible as to the critical cooling rate, it is presumable that a micro amount of various elements partially acts as a controlling factor in this respect.

Fig. 5 shows the Ms points of Fe-C alloys(11) that have been obtained by many workers. Their mean (mean of the curve band in the figure) was adopted as Ms

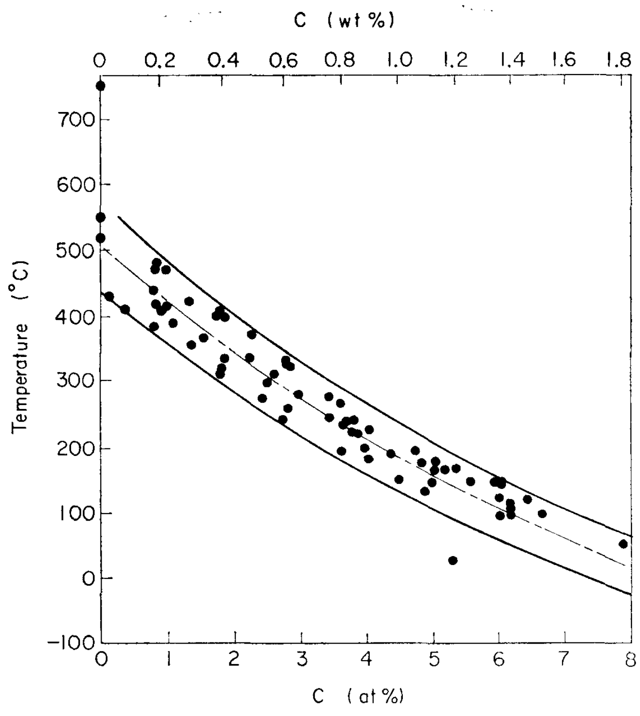


Fig. 5. Ms temperature of iron-carbon alloy.

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(6) P. Lehr, Compt. Rend., **242** (1956), 632.
(7) E. Eichen and J.W. Spretnak, Trans. ASM, **51** (1959), 454.
(8) F.S. Buffington, K. Hirano and M. Cohen, Acta Met., **9** (1961), 434.
(9) A. Gilbert and W.S. Owen, Acta Met., **10** (1962), 45.
(10) S. Tawara, J. Iron & Steel Inst. Japan, **23** (1938), 875.
(11) M. Tsuchiya, M. Izumiyama and Y. Imai, J. Japan Inst. Metals, **29** (1965), 427.

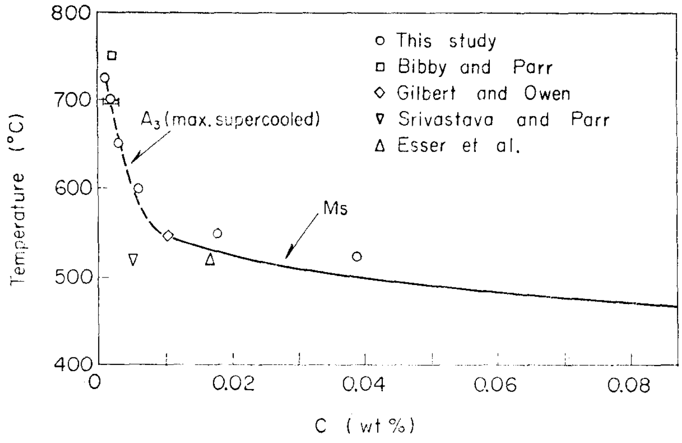

Fig. 6. Ms and maximum supercooled A_3 temperature of iron-low carbon alloy.

point of Fe-C alloy containing less than 0.1 wt% C, and this is shown in Fig. 6 together with the result of the present study. As evident in the figure, the Ms point at high carbon concentration, when extrapolated to C%=0, becomes about 550°C, while in the present study, the point sharply rises in the case of the alloy containing less than 0.006 wt%C. The transformation point showing this sharp rise has been considered as Ms point by Parr et al.(5) but at the present stage at which exact conditions of martensitic transformation remain uncertain, it may be valid to consider that this is a supercooled A_3 transformation initiated partially by diffusional process and partially by shearing mechanism.

2. Fe-Ni binary alloys

Figs. 7~9 show effects of cooling rate on A_3 points of Fe-Ni binary alloys. Similar to the case of Fe-C system, A_3 point gradually lowers as the cooling rate

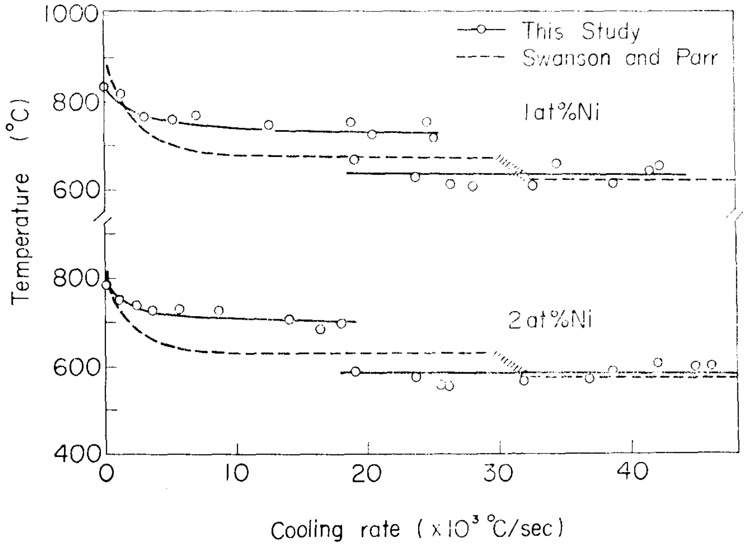

Fig. 7. Effect of cooling rate on transformation temperature of Fe–1 at% Ni and Fe–2 at% Ni alloys.

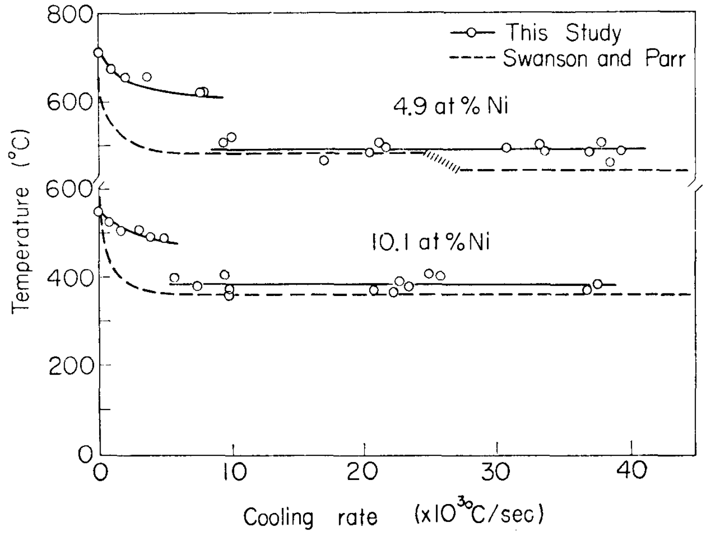

Fig. 8. Effect of cooling rate on transformation temperature of Fe–5 at% Ni and Fe–10 at% Ni alloys.

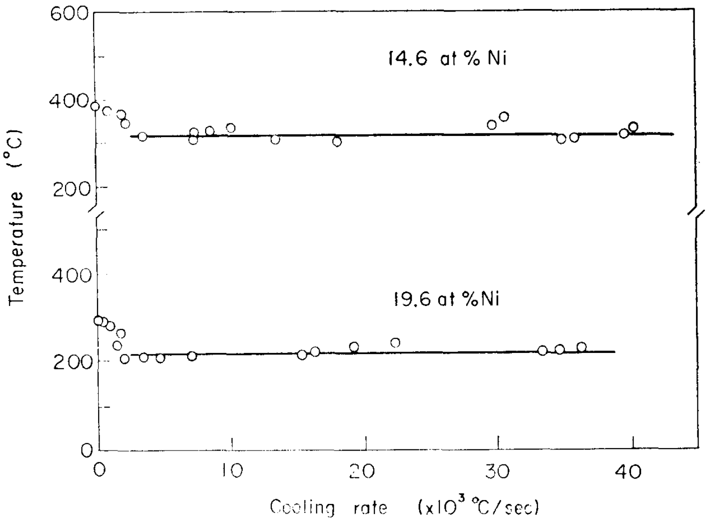

Fig. 9. Effect of cooling rate on transformation temperature of Fe–15 at% Ni and Fe–20 at% Ni alloys.

increases, and shown a discontinuous fall at a certain cooling rate, but after this fall it remains constant and never falls lower even if the cooling rate is increased further. These behaviors correspond respectively to the transformation at higher temperatures and that at lower temperatures of iron-low carbon alloys containing over 0.006 wt%C. That is, the transformation that occurs in alloys of Fe-Ni system at a lower temperature is considered to show a martensitic transformation. Also, an examination of Fe-Ni specimens transformed at lower temperatures has resulted in showing a martensitic rugged surface usually observable in Fe-C alloys.

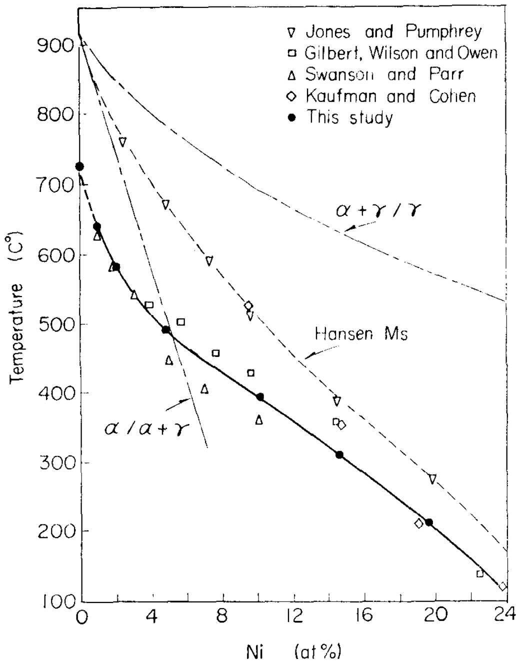

Fig. 10. Ms temperature of iron-nickel binary alloy.

Fig. 10 shows the relation between the transformation point of Fe-Ni alloys at lower temperature and the content of nickel. The alloys containing higher nickel show little difference between the transformation point and the Ms point formerly obtained at low cooling rates(12),(13), but this difference becomes larger as the nickel content becomes lower. Also in the figure are shown Ms points recently obtained by other workers at high cooling rate(1),(2),(9), which agree well with the transformation points in the present study. Then, when the Ms point of Fe-Ni alloy shown as a function of nickel content is extrapolated to Ni%=0, Ms point of pure iron can be shown to be about 720°C as can be seen in Fig. 10, which accords with the maximum supercooled A_3 point of pure iron. Swanson and Parr(1), as the result of the extrapolation, estimated Ms point of pure iron at 680°C. However, in view of the fact that the extrapolation for this purpose needs a considerable number of measuring points, and that the curve obtained shows a very sharp slope, it is considered uncertain to estimate, at this stage, Ms point of pure iron by means of extrapolation.

In order to examine characteristics of supercooled A_3 transformation, shown in Figs. 7~9, continuous cooling transformation curves (CCT) were obtained and therewith isothermal transformation curves (TTT) were drawn by the method of Grange and Kiefer(14). An example of the curves obtained is shown in Fig. 11, which shows that the isothermal transformation curve of this alloy, Fe-10.1 at%

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(12) F.W. Jones and W.I. Pumphrey, J. Iron Steel Inst., **163** (1949), 121.
(13) L. Kaufman and M. Cohen, J. Metals, **8** (1956), 1393.
(14) R.A. Grange and J.M. Kiefer, Trans. ASM, **29** (1941), 85.

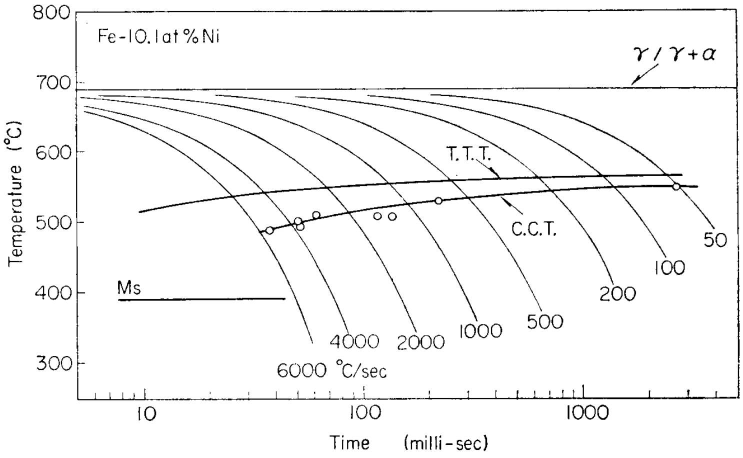

Fig. 11. CCT and TTT diagrams of Fe–10 at% Ni alloy.

Ni, lowers very slowly toward the short-time side. This causes the effect of cooling rate on the transformation temperature to appear extremely slow and eventually makes the transformation temperature seem to remain almost stationary even if the cooling rate is somewhat changed. It was for this reason that previous workers⁽¹²⁾ were confused in considering that the transformation temperature of Fe-Ni alloy was constant within the range of cooling rates of 2°~150°C/min. It has also been found that the C-curve of supercooled A_3 transformation of Fe-Ni binary alloy moves toward the long-time side as well as toward the low-temperature side as the nickel content increases.

Summary

By using a gas quench apparatus, the effect of cooling rate on A_3 transformation was examined on various kinds of iron varying in purity and on Fe-Ni binary alloys within the range of cooling rates at 100°~60,000°C/sec. The results obtained are summarized as follows:

(1) A_3 point of iron containing less than 0.003 wt% carbon gradually lowers as the cooling rate increases and remains stationary over the range of 15,000°~30,000°C/sec. On the other hand, in iron containing over 0.006 wt% carbon it gradually lowers as the cooling rate increases, but within the range of 20,000~30,000°C/sec it falls discontinuously and thence remains stationary even if the cooling rate is further increased.

(2) Maximum supercooled A_3 point of iron receives a great influence by a slight change in carbon content, falling down to about 720°C with 0.001 wt% carbon and to about 650°C with 0.003 wt% carbon.

(3) A_3 point of Fe-Ni binary alloy gradually lowers as the cooling rate increases. Irrespective of the composition, the transformation point of this system falls discontinuously at a certain cooling rate, and thence remains con-

stant even if the cooling rate is further increased. This critical cooling rate lowers as the nickel content increases.

(4) The transformation point that has lowered discontinuously agrees with the Ms point formerly obtained at a slow cooling rate, in case the nickel content is high, but it falls considerably lower than the point formerly measured, in case the nickel content is low.

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