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Effects of Alloying Element on Supercooled A_3 Transformation of Iron*

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Synopsis

The cooling rate dependence of A_3 transformation and the maximum supercooled A_3 point have been examined on eleven kinds of iron binary alloy by using a rapid cooling apparatus. Maximum supercooled A_3 points of Fe-Mn alloys show good agreement at higher manganese concentrations with those reported previously but are displaced to lower temperatures at lower manganese concentrations. Extrapolation of the data zero content of the alloying element leads to the maximum supercooled A_3 point of about 720°C for pure iron. The maximum supercooled A_3 points of Fe-Cr, Fe-Cu and Fe-Mo alloys descend with increasing content of alloying element and those of Fe-Al, Fe-Ti and Fe-V alloys ascend. In Fe-Co alloys, the maximum supercooled A_3 point rises up to about 40% Co and then lowers. Si, W and Nb have little effect on the maximum supercooled A_3 temperature of iron. Some of the alloying elements have a different effect on the change of A_3 point of iron with concentration both in the non-equilibrium and in the equilibrium condition.

I. Introduction

Many studies hitherto performed concerning effects of various alloying elements on the transformation of quenched steel have served to understand the roles of these elements⁽¹⁾. However, these data have all concerned with the function of the third element coexisting with carbon, and eventually included a certain effect of interaction with carbon. Therefore, these data can be approximately significant only when this effect is negligibly small, while, when the effect is considerably large, they may remain so much away from showing the intrinsic function of alloying elements. In the present study, with the aim of throwing light on intrinsic features of the effects of various alloying elements upon transformation of steel, high-purity iron binary alloys were rapidly quenched, and the maximum supercooled A_3 points were measured.

II. Experimental method

Electrolytic iron and high-purity metals were prepared for specimens of various iron binary alloys by the same method and procedure as in the preceding

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* The **1464th** report of the Research Institute for Iron, Steel and Other Metals. Published in Japanese in the J. Japan Inst. Metals, **34** (1970), 291.

(1) Gakushin Committee, Editing, *Steel and Alloying Elements*, (1966).

Table 1. Chemical composition of various iron binary alloys (wt%)

Alloy	Mn	C	N
Fe-Mn	1.11	0.002	0.003
	2.27	0.002	0.004
	3.41	0.002	0.004
	4.68	0.003	0.002
	7.27	0.002	0.003
	9.47	0.002	0.003
	Co	C	N
Fe-Co	5.98	0.004	<0.001
	14.35	0.003	0.001
	24.09	0.002	<0.001
	35.47	0.006	0.001
	48.56	0.004	<0.001
	59.17	0.008	—
	Cr	C	N
Fe-Gr	1.01	0.002	0.002
	2.09	0.004	0.002
	4.06	0.003	0.001
	6.20	0.005	0.001
	7.97	0.004	0.001
	9.98	0.004	0.001
	Ti	C	N
Fe-Ti	0.05	0.003	0.002
	0.16	0.004	0.002
	0.25	0.002	0.002
	0.34	0.003	0.002
	0.44	0.003	0.003
	0.52	0.003	0.002
	V	C	N
Fe-V	0.09	0.003	0.002
	0.29	0.002	0.002
	0.48	0.003	0.002
	0.68	0.003	0.002
	0.86	0.003	0.003
	1.06	0.003	0.003

Alloy	Cu	C	N
Fe-Cu	0.95	0.003	0.001
	1.90	0.004	0.001
	2.83	0.004	0.001
	3.52	0.003	0.001
	4.69	0.003	0.002
	Mo	C	N
Fe-Mo	0.38	0.002	0.002
	0.77	0.002	0.002
	1.12	0.002	0.002
	1.50	0.002	0.002
	1.91	0.003	0.003
	W	C	N
Fe-W	0.48	0.002	0.003
	0.96	0.003	0.004
	1.43	0.004	0.046
	1.92	0.004	0.026
	2.32	0.002	0.009
	2.83	0.002	0.007
	Nb	C	N
Fe-Nb	0.09	0.002	0.002
	0.19	0.002	0.003
	0.39	0.003	0.002
	0.60	0.003	0.003
	0.80	0.003	0.002
	0.99	0.003	0.002
	Al	C	N
Fe-Al	0.071	0.002	0.001
	0.14	0.002	0.001
	0.25	0.002	0.001
	0.35	0.001	0.001
	Si	C	N
Fe-Si	0.37	0.003	0.001
	0.82	0.002	0.002
	1.28	0.003	0.001

case(2). Metals used in the present case were Mo, Co, Ti, V, W, and Nb, all of 99.9 per cent, and Mn, Cr, Al, Cu, and Si, all of 99.99 per cent in purity. For homogenizing, Fe-Mn alloy was annealed in a dry hydrogen atmosphere at 1200°C for 8 hrs, and the other alloys in vacuum at 1000°C for 2 hr. The results of chemical analyses of specimens are shown in Table 1.

The methods of quenching and of measuring transformation point and the dimension of specimens were the same as those in the preceding case(2). The auste-

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(2) M. Izumiyama, M. Tsuchiya and Y. Imai, J. Japan Inst. Metals **34** (1970) 286: Sci. Rep. RITU, **A 22** (1970), 93.

nitizing temperature was 1000°C for Fe-Mn, Fe-Cr, and Fe-Cu alloys, 1050°C for Fe-Co alloy, and 1100°C for other alloys. No effect of austenitizing temperature upon transformation points has been observed in any alloys containing no carbon of the same system within the range of 1000°~1100°C. Specimens were held for 30 sec at the austenitizing temperature.

III. Results and discussion

1. Fe-Mn and Fe-Cu alloys

Figs. 1 and 2 show the relation between transformation point and cooling rate respectively for Fe-Mn and Fe-Cu alloys, showing that transformation points

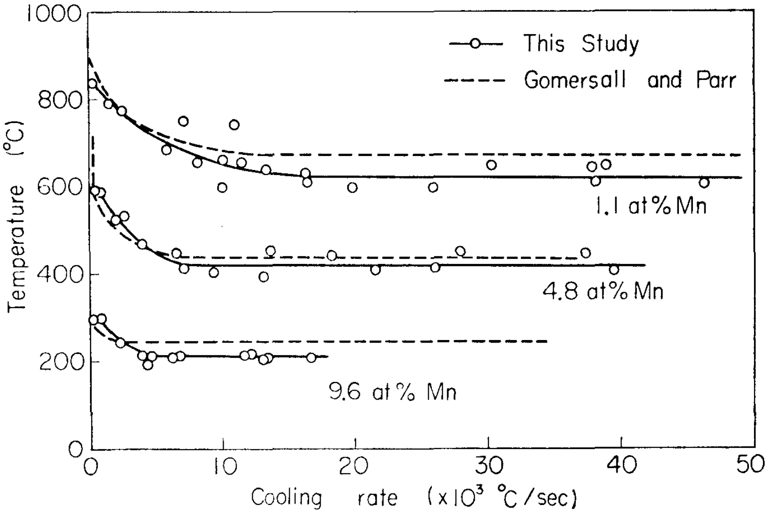

Fig. 1. Effect of cooling rate on transformation temperatures of Fe–1 at% Mn, –5at% Mn and –10at% Mn alloys.

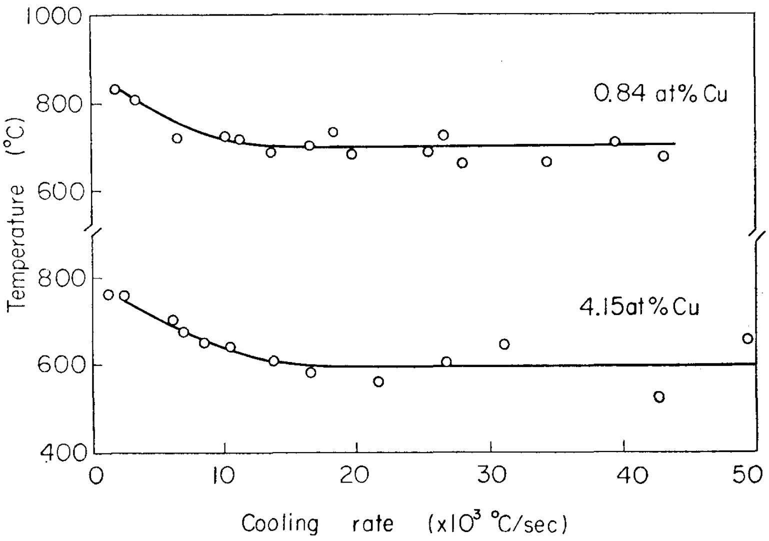

Fig. 2. Effect of cooling rate on transformation temperatures of Fe–1 at% Cu and –4at% Cu alloys.

of alloys of these systems gradually lower as the cooling rate increases, and that after certain points they remain stationary without influence from the cooling rate. In the case of Fe-Ni alloy, as shown in the precedingr report(2), the transformation point gradually lowered as the cooling rate increased, and showed a discontinuous fall at a certain cooling rate, but in the present cases of Fe-Mn and Fe-Cu alloys, no such fall was observed. Transformation points of these alloys different in the composition were measured and their maximum supercooled A_3 points were determined therewith to obtain the relation of these A_3 points to the content of Mn and that of Cu. The results obtained with Fe-Mn alloys are shown in Figs. 3 including those obtained by other workers(3)~(6) with Fe-Mn alloy. The transformation points of Fe-Mn alloy obtained in the present study agree with those obtained by means of high cooling rate by Gomersall and Parr(5), but, at low Mn content, a disagree with the results has been obtained by Jones and Pumphrey(3), and by Troiano and McGuire(4), perhaps because of their transformation points being not identical with maximum supercooled A_3 points. The maximum supercooled A_3 points of Fe-Mn alloy determined in the present study, when extrapolated to Mn=0, agree well with that of the pure iron containing 0.001% C shown in the preceding report.

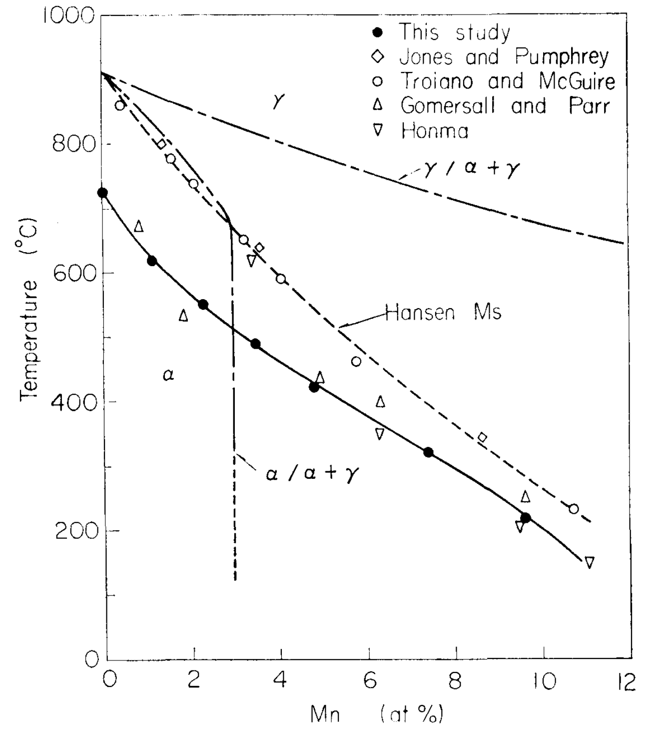

Fig. 3. Maximum supercooled A_3 temperature of iron-manganese binary alloy.

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(3) F.W. Jones and W.I. Pumphrey, J. Iron Steel Inst., **163** (1949), 121.
(4) R.A. Troiano and F.T. McGuire, Trans. ASM, **31** (1943), 340.
(5) D.W. Gomersall and J.G. Parr, J. Iron Steel Inst., **203** (1965), 275.
(6) T. Honma, Denki Seiko, **30** (1959), 319.

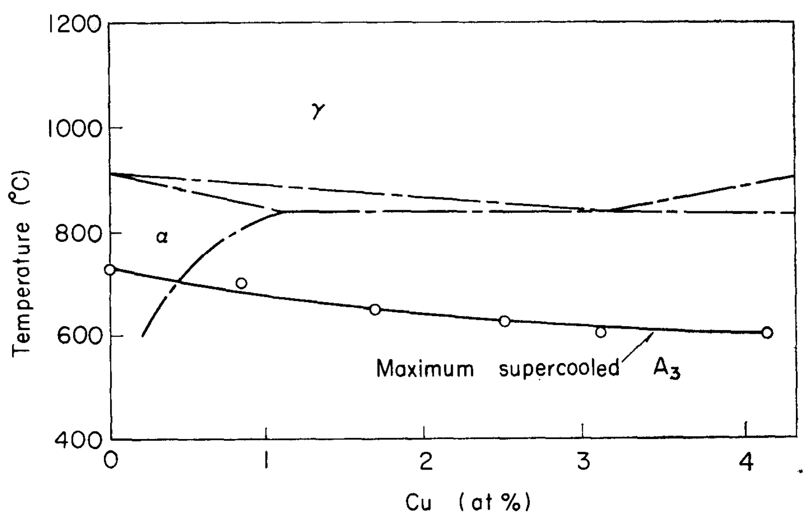

Fig. 4. Maximum supercooled A_3 temperature of iron-copper binary alloy.

Maximum supercooled A_3 points of Fe-Cu alloys lower as Cu content increases as shown in Fig. 4.

2. Fe-Co alloy

Fig. 5 shows the relation between transformation points and cooling rates of Fe-Co alloys. In the alloys of this system, transformation points have not been observed separately at two levels. Parr⁽⁷⁾, in his study on Fe-Co alloys containing 0.1~0.5% cobalt, has observed the transformation point at two levels. However, carbon content in the pure iron used by Parr was 0.009 per cent, and

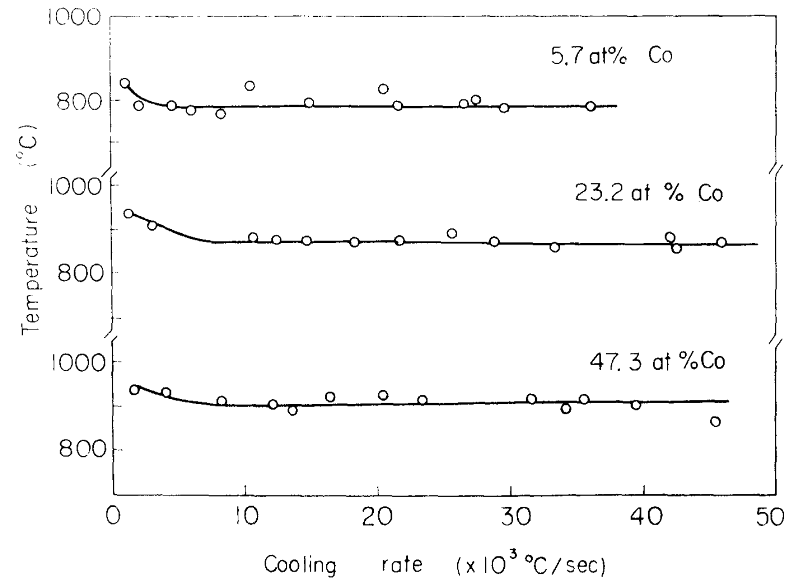

Fig. 5. Effect of cooling rate on transformation temperatures of Fe–6at% Co, –23at% Co and –47at% Co alloys.

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(7) J.G. Parr, J. Iron Steel Inst., **205** (1967), 426.

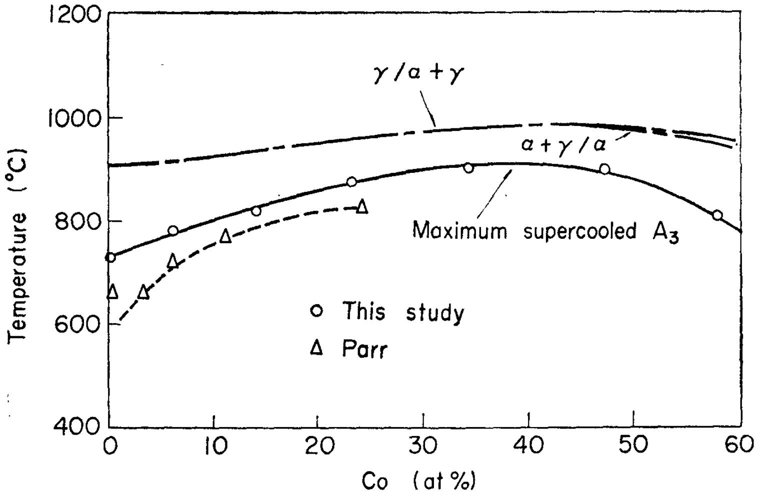

Fig. 6. Maximum supercooled A_3 temperature of iron-cobalt binary alloy.

it seems probable that his finding has resulted from the effect of carbon rather than that of cobalt, for, as previously mentioned, when carbon content is over 0.006 per cent, the transformation takes place at two steps of temperature. Fig. 6 shows the relation between the maximum supercooled A_3 point and the content of cobalt in alloys of this system, showing that these A_3 points show almost the same tendency as the boundary of $\gamma/\gamma+\alpha$ phase, rising up until about 40 at% Co and falling thence with higher content of cabalt. In Fig. 6 is included the result of Parr's study which shows that, up to about 1% Co, Ms point sharply falls down to about 600°C, as cobalt content is increases, and then rises discontinuously. This sharp fall of Ms point, as previously described, is considered to be due to the dominant effect of carbon over that of cobalt. The maximum supercooled A_3 point of Fe-Co alloy, resulted from the present study when the cobalt content is reduced to zero, accords with that of the pure iron containing 0.001 wt% C as shown in the preceding report(2).

3. Fe-Cr alloy

Fig. 7 shows the relation between the effect of cooling rate upon transformation point and the content of chromium in Fe-Cr alloy. Similar to the preceding case of Fe-Ni system(2), Fe-Cr alloys containing a low amount of chromium show, in general, transformation points at two levels, but as chromium content becomes high, this separation becomes indistinct.

Fig. 8 shows the relation of the maximum supercooled A_3 point to the content of chromium in Fe-Cr alloy, including the results obtained by other workers.(8)~(11)

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(8) A. Gilbert and W.S. Owen, Acta Met., **10** (1962), 45.
(9) J.M. Wallbridge and J.G. Parr, J. Iron Steel Inst., **204** (1966), 119.
(10) E.A. Wilson, Ph. D. Thesis, Univ. Of Liverpool, (1964).
(11) J.S. Pascover and S.V. Radcliffe, Trans. Met. Soc. AIME, **242** (1968), 673.

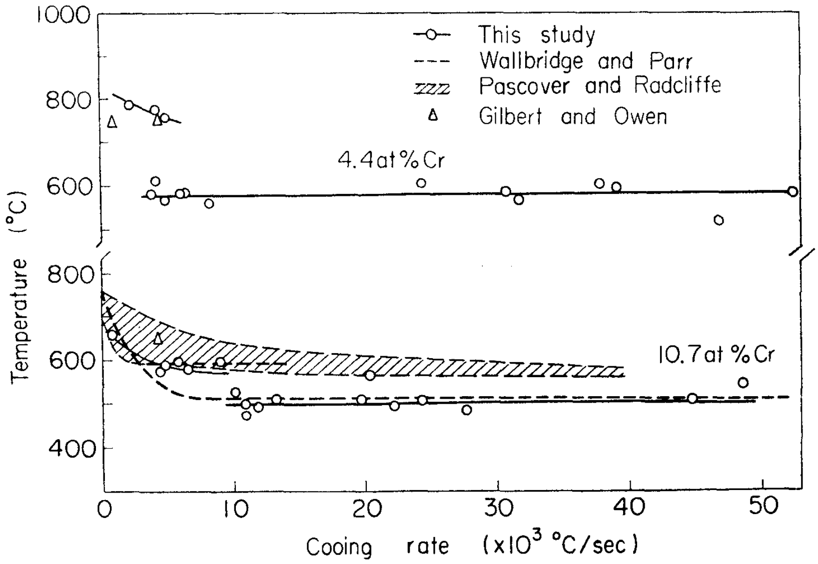

Fig. 7. Effect of cooling rate on transformation temperatures of Fe-4.5 at% Cr and -11at% Cr alloys.

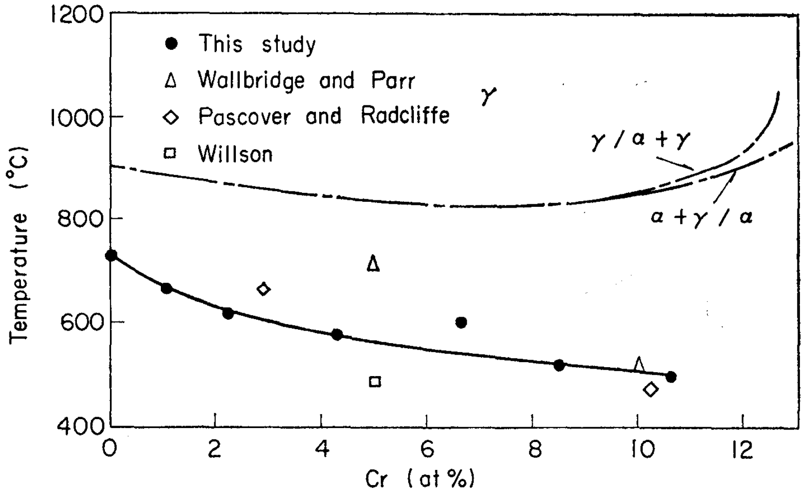

Fig. 8. Maximum supercooled A_3 temperature of iron-chromium binary alloy.

In the equilibrium phase diagram, chromium is known⁽¹²⁾ as a γ-loop forming element which reduces the austenite and expands the ferrite region, but in the case of phase change in unequilibrium state, it forms no loop and acts to lower the maximum supercooled A_3 point. This is certainly a very interesting function of this element, which will be discussed in the ensuing report.

4. Other alloys

Figs. 9 and 10 show the effects of cooling rates on transformation temperatures of iron base binary alloys containing Si, Al, Ti, W, V, Mo, and Nb, respectively. In either of these alloys such two kinds of transformation point

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(12) M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958).

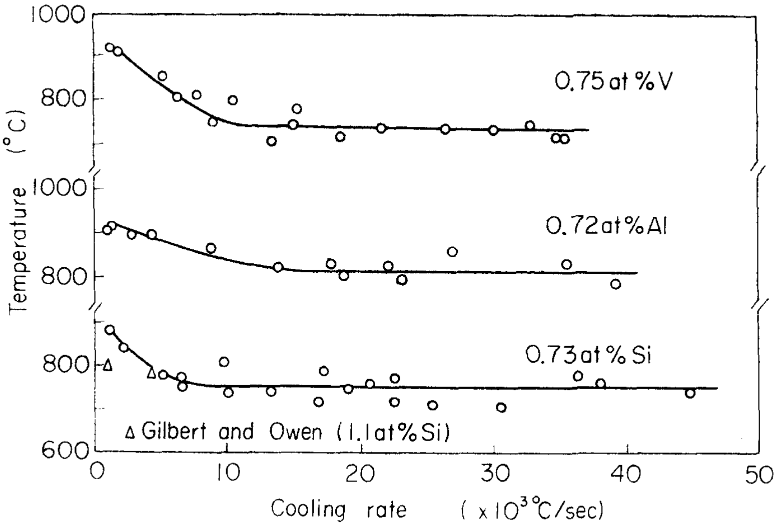

Fig. 9. Effect of cooling rate on transformation temperatures of Fe-V, Fe-Al and Fe-Si alloys containing 0.7at% alloying element, respectively.

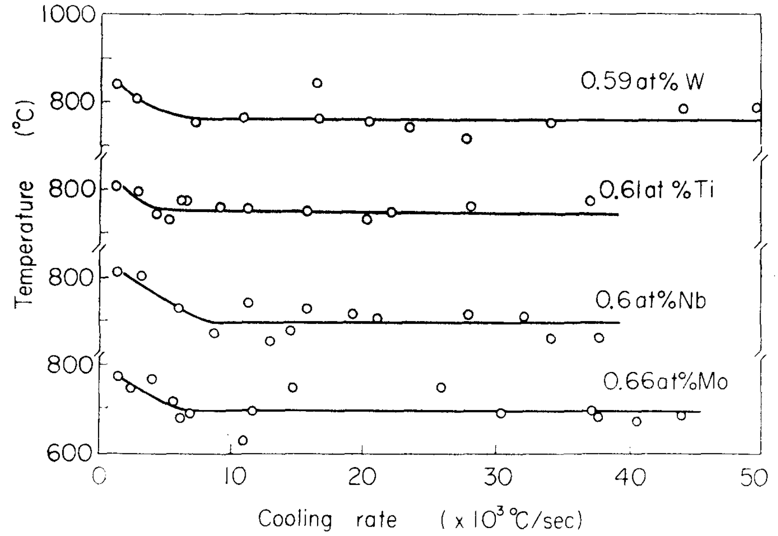

Fig. 10. Effect of cooling rate on transformation temperatures of Fe-W, Fe-Ti, Fe-Nb and Fe-Mo alloys containing 0.6 at% alloying element, respectively.

that were observed in Fe-C and Fe-Ni alloys in the preceding case(2) were not observed. Although no distinct systematical regularity was discernible in the dependence of critical cooling rate of these alloys upon the concentration of alloying element, Fe-Nb and Fe-Si alloys both showed this dependence comparatively clear in tendency. In the case of Fe-Nb alloy, as alloying element increases the critical cooling rate becomes small, while this rate contrarily becomes large in the case of Fe-Si alloy. Gilbert and Owen's data(8) of Fe-Si alloy, also shown in Fig. 9. Figs. 11 ~ 13 show maximum supercooled A_3 points of various binary alloys as functions of the concentration of alloying elements. The maximum supercooled A_3 points of almost all of these alloys rise corresponding to γ-loop, or at least

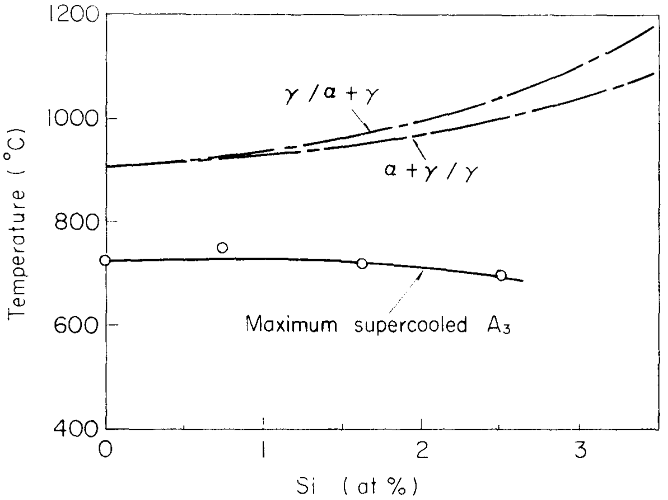

Fig. 11. Maximum supercooled A_3 temperature of iron-silicon binary alloy.

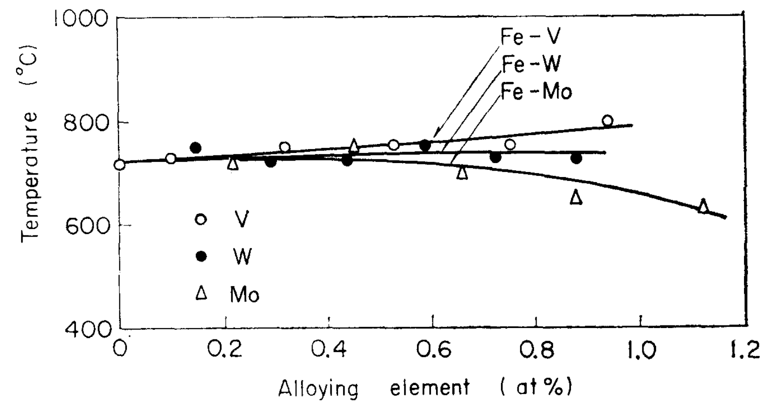

Fig. 12. Maximum supercooled A_3 temperature of Fe-V, Fe-W and Fe-Mo alloys.

remain constant with the increase in alloying element, with the exceptions of Fe-Mo and Fe-Si alloys, in both of which the points contrarily fall in the range of high content of alloying element. A property of molybdenum that acts in steel to lower Ms point remarkably was similarly observed in the present experiment of Fe-Mo binary alloy. Including the results in the preceding case(2), Ms points or maximum supercooled A_3 points of iron binary alloys are collectively shown in Fig. 14. In general, the Ms point or the maximum supercooled A_3 point lowers with the increase in alloying element for γ-open alloys (Fe-Ni and Fe-Mn systems) and γ-expanded alloys (Fe-C and Fe-Cu systems), while for γ-closed alloys (Fe-Al, Fe-V, Fe-W, and Fe-Ti systems), and γ-reduced alloy (Fe-Nb system), the maximum supercooled A_3 point shows a tendency to rise with the increase in alloying element. Fe-Co alloys, categorically of γ-releasing type, show a special feature in the behavior of A_3 transformation point, which rises with the increase in cobalt content up to 40 per cent, and then falls. The same tendency is followed by their maximum supercooled A_3 points, which accord with the results presumable

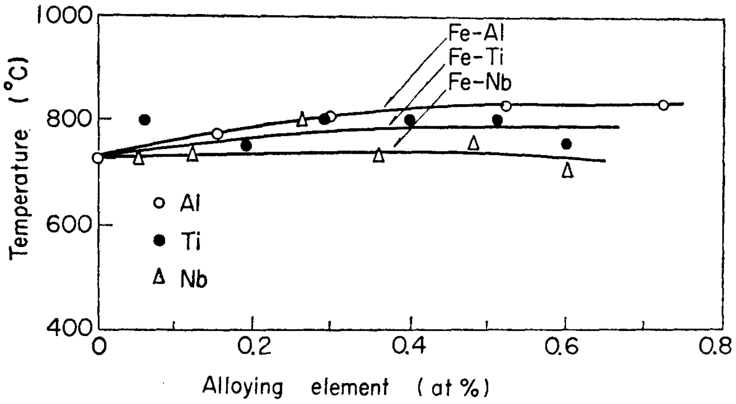

Fig. 13. Maximum supercooled A_3 temperature of Fe-Al, Fe-Ti and Fe-Nb alloys.

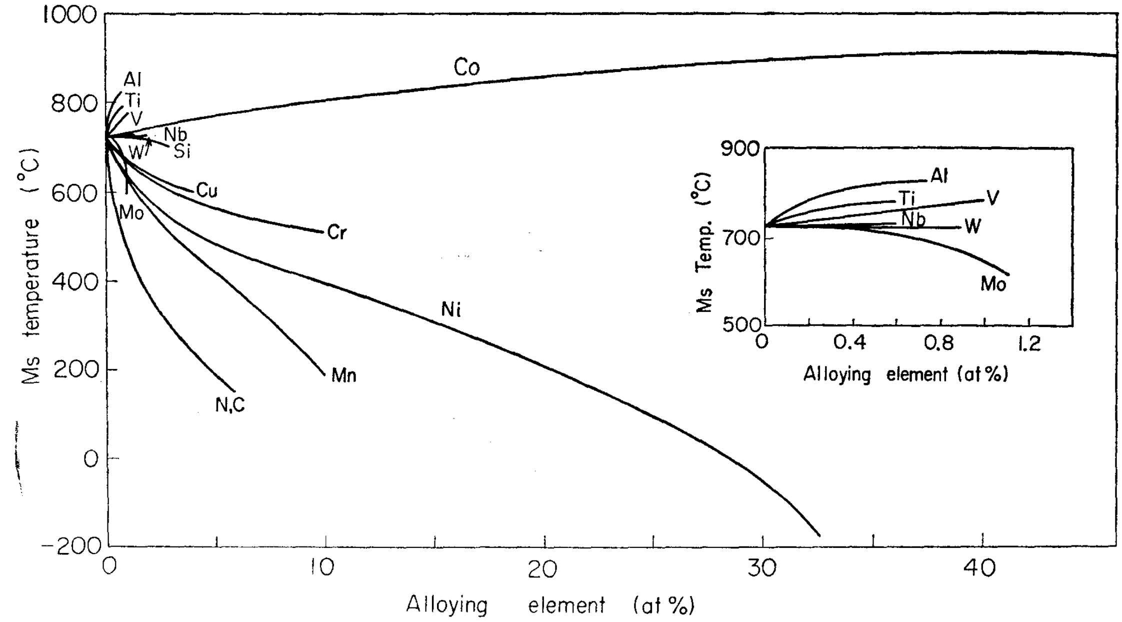

Fig. 14. Effect of alloying elements on Ms or maximum supercooled A_3 temperature of iron.

from the costitutional diagram of binary alloys. In Fe-Cr alloys it is also presumed from the phase diagram to show a tendency in which the A_3 transformation point once falls and then rises just contrary as in the case of Fe-Co system, but the maximum supercooled A_3 point constantly falls with the increase in chromium. In case of Fe-Si and Fe-Mo system shows a sharp lowering of Ms temperature which makes it impossible to presume from the constitutional diagram of binary alloys.

As shown in Fig. 14, the most influential of these elements are of interstitial type C(2) and N(13), while the most influential element in alloys of substitutional type is manganese which is known as the most favorable element to raise the

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(13) Y. Imai, M. Izumiyama and M. Tsuchiya, Sci. Rep. RITU, A **17** (1965), 173.

hardenability of steel. Tungsten and vanadium which are both considered as elements to lower Ms point in steel have not always shown the same effect in pure iron on the maximum supercooled A_3 point. It is indeed improper to compare the case of steel with present case of pure iron, because the former is concerned with the effect of alloying element on martensitic transformation in presence of carbon. That is, viewed from the result of the present study and also from the fact that tungsten and vanadium in steel have also caused Ar' point to lower(14), it seems probable that the functions of tungsten and vanadium observed in steel have, in fact, been helped substantially by the effect of carbon. Indeed in steels containing tungsten, vanadium or titanium there is a maximum point of hardenability at some percent then slow down as increase of these elements. The result of the present study may give evidence that the functions of various alloying elements hitherto observed in steel should be considered always connected with carbon.

Summary

By using a gas quenching apparatus, the dependence of A_3 point upon cooling rate was examined with iron binary alloys containing respectively aluminium, chromium, cobalt, copper, manganese, molybdenum, niobium, silicon, titanium, tungsten and vanadium, and each maximum supercooled A_3 point was determined. The results obtained are summarized as follows:

(1) Maximum supercooled A_3 point of Fe-Mn binary alloy agrees with the result obtained formerly, at a high concentration of manganese, while, at a low concentration, the point falls appreciably lower than the former result. The maximum supercooled A_3 point of Fe-Mn alloy obtained when extrapolated to Mn %=0, becomes about 720°C, agreeing with the point of pure iron (containing 0.001 %C).

(2) Maximum supercooled A_3 points of Fe-Cr, Fe-Cu and Fe-Mo alloys fall, while those of Fe-Al, Fe-Ti ,and Fe-V alloys rise, as alloying elements increase.

(3) The maximum supercooled A_3 point of Fe-Co alloy rises as the content of cobalt increases up to 40 per cent, and thence falls with the increase in cobalt. Maximum supercooled A_3 points of Fe-Si, Fe-W, and Fe-Nb show almost no change with the concentration of alloying elements.

(4) Some of these alloying elements show different effects upon A_3 points of iron presumed from equilibrium condition.

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(14) S. Tawara, J. Iron Steel Inst. Japan, **23** (1938), 875.