Relationship between the Solid Phase Equilibrium and the Isothermal Martensite Transformation in Fe-Ni-Cr and Fe-Ni-Mn Alloys

Relationship between the Solid Phase Equilibrium and the Isothermal Martensite Transformation in Fe-Ni-Cr and Fe-Ni-Mn Alloys*

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    The change in free-energy attendant upon the athermal and the isothermal transformations of austenite into martensite in Fe-Ni-Cr and Fe-Ni-Mn alloys was investigated. In Fe-Ni-Cr alloys containing 17 weight % Cr, the driving force necessary to initiate the athermal martensite transformation increases as Ni content increases, whereas in the isothermal transformation, this force decreases. When the Ni content in the alloys exceeds about 7 weight %, the martensite is formed isothermally at a temperature above M_s point and the driving force at this point is about 490 cal/mole. Similar phenomena were also observed in Fe-23% Ni-Mn alloy. In this alloy, the martensite is formed isothermally at a temperature above M_s point when the Mn content exceeds about 3.5 weight % and the driving force at this critical point is about 430 cal/mole. Temperatures for maximum rates of the isothermal martensite transformation in Fe-Ni-Cr and Fe-Ni-Mn alloys lower with the increases of Ni and Mn content, respectively. The driving forces for the athermal martensite transformation in the Fe-Ni-Cr and the Fe-Ni-Mn alloys used in the present work are larger than that of other alloys in which the martensite is formed only athermally. From these results, it is suggested that the nucleus of new phase in isothermal martensite transformation cannot develop into martensite plate only by the stored free energy, but probably some thermal fluctuation will play an important role.

I. Introduction

It has been known that the transformation of austenite into martensite in steels occurs so rapidly that it is not suppressed even by drastic quenching, and that the transformation will not further proceed though the steel is allowed to remain at a temperature at which the transformation occurs in quenching. These facts have been regarded as important characteristics of this transformation. Thereafter, Kurdjumov and Maksimova[1][2] have discovered the isothermal martensite transformation in Mn steels and Fe-Ni-Mn alloys, which has exerted a great influence on the mechanism of the martensite transformation, especially in kinetics and thermodynamics. At an early stage, however, no attention was paid to the presence of such a martensite, because the amount of transformation was small and because it was considered to be a continuation of athermal martensite formed ɪby quenching. Afterwards, isothermal martensite transformation has been observed in many

(1) G.V. Kurdjumov and O.P. Maksimova, Dokl. Akad. Nauk, SSSR, **61** (1948), 83.
(2) G.V. Kurdjumov and O.P. Maksimova, Dokl. Akad. Nauk, SSSR, **73** (1950), 95.

alloys, and it has been made clear that in certain alloys the latter martensite covers most of that part. Hence, it is of importance to clarify the relation between the two kinds of martensite not only from the theoretical point of view but also from the practical side.

In general, an excessive free energy which is required to resist the transformation strain must be stored, since the martensite transformation induces a large strain. Now, no transformation of martensite occurs at temperature T_0 at which $-\Delta F^{\gamma \to \alpha'}=0$, i.e. at the metastable equilibrium temperature between austenite and martensite, the austenite being supercooled to the beginning temperature of martensite transformation, that is, to M_s point. The stored free energy caused by this supercooling will then play the role of the driving force which is necessary to initiate the transformation of austenite into martensite. That is to say, the thermodynamical treatment of the transformation of austenite into martensite is to determine the degree of supercooling from T_0 to M_s, and to obtain the amount of free energy which is stored by this supercooling.

Consequently, if these values are determined, a key will be secured to solve the relation between the athermal and the isothermal martensite transformation.

II. Specimens and experimental method

The compositions of specimens, 3 alloys of Fe-Ni-Cr system and 4 alloys of Fe-Ni-Mn system, are shown in Table 1. They were drawn into wires of 1 mm $\phi \times$

Table 1. Chemical composition, wt. %

Specimen No.	C	N	Si	Mn	P	S	Ni	Cr
1	0.10	0.005	0.30	0.40	<0.005	<0.015	4.00	17.0
2	0.11	0.005	0.33	0.38	<0.005	<0.015	7.25	15.6
3	0.11	0.005	0.29	0.44	<0.005	<0.015	8.18	16.93
4	0.016	0.003	0.38	2.23	0.008	0.009	23.47	—
5	0.008	0.001	0.33	2.40	0.004	0.010	23.04	—
6	0.010	0.005	0.43	2.71	0.004	0.013	22.94	—
7	0.005	0.002	0.41	2.85	0.004	0.010	23.34	—

100 mm l, and were water quenched from 1150°C and kept isothermally in a low-temperature bath. The amount of isothermal martensite transformation was estimated from the measurement of electrical resistance. The time of isothermal transformation was measured after the specimen was kept for one minute in the low-temperature bath. The relationship between the change in electrical resistance and the amount of transformation was determined by the same method as in the previous case[3]. As a result, it was found that in every alloy an increase of 1% in electrical resistance corresponded to about 2% of martensite transformation, showing quite a good linear relationship. Ethyl alcohol was used in the bath, the holding temperature being controlled with liquid-air.

    (3) H.C. Fiedler, B.L. Averbach and M. Cohen, Trans. ASM, 47 (1955), 267.

III. Results

1. Fe-Ni-Cr alloys

The change in free energy accompanying the martensite transformation of Fe-Ni-Cr alloys was calculated by Kaufman[4] as follows:

$$\Delta F^{\alpha' \to \gamma} = (1 - x - y)\,(1202 - 2.63 \times 10^{-3}\,T^2 + 1.54 \times 10^{-6}\,T^3)$$
$$+ y\,(460 + 1.0T) + x\,(- 3700 + 7.09 \times 10^{-4}\,T^2 + 3.91 \times 10^{-7}\,T^3)$$
$$+ y\,(1 - x - y)\,(- 2800 + 0.75\,T) + x\,(1 - x - y)$$
$$\times\, [3600 + 0.58\,(1 - l\,n\,T)]\ \text{cal/mole}\,, \tag{1}$$

where x and y represent the atomic fraction of Ni and Cr, respectively, and T the absolute temperature.
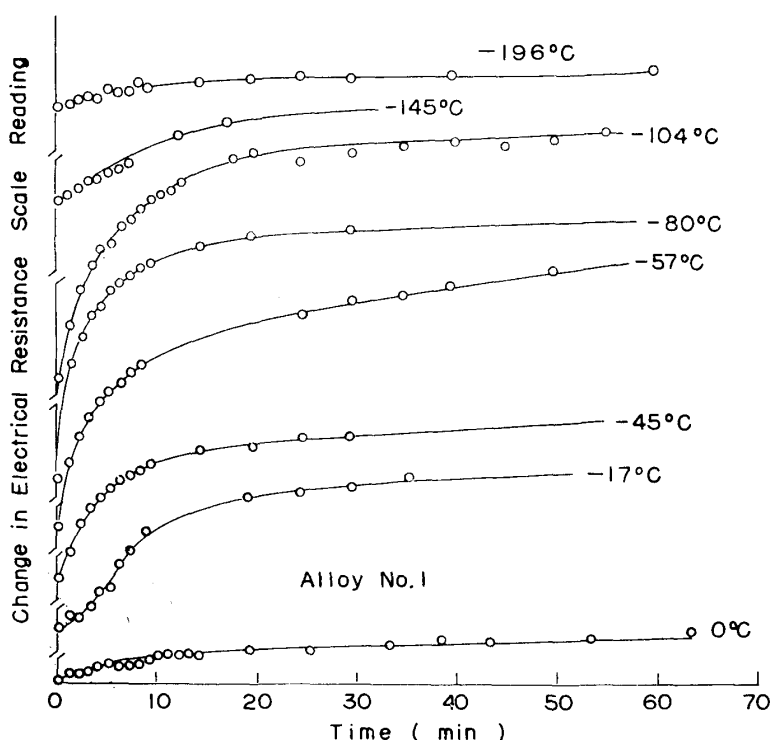
Fig. 1. Change in electrical resistance for alloy No. 1 due to isothermal transformation of austenite to martensite at various sub-atmospheric temperature.

Fig. 1 shows the transformation curves of alloy No. 1, in which the isothermal martensite transformation takes place. These curves show the relations between the change in electrical resistance due to isothermal transformation and the time of isothermal keeping at various low temperatures. As shown in the figure, the change in electrical resistance at $-80°C$ is maximum. Fig. 2 shows a T.T.T. diagram of the isothermal martensite transformation derived from Fig. 1. As seen in the figure, the curves of isothermal transformation of the alloy No. 1 are of C-type with

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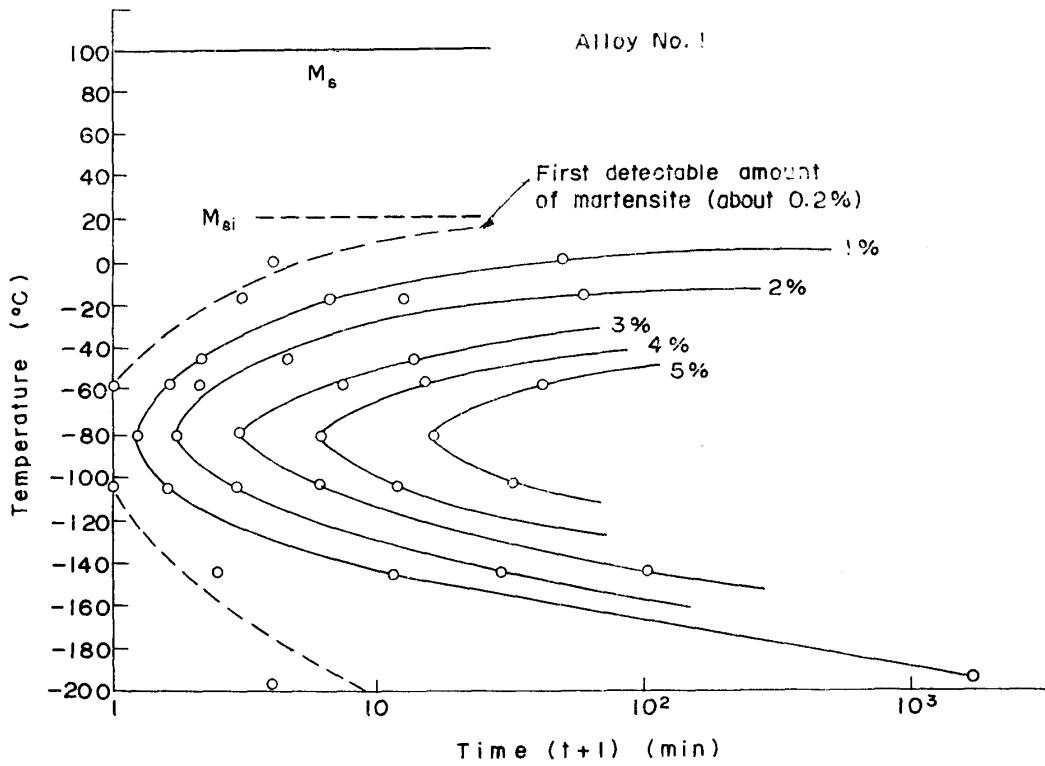(4) L. Kaufman, Trans. AIME, **215** (1959), 218.

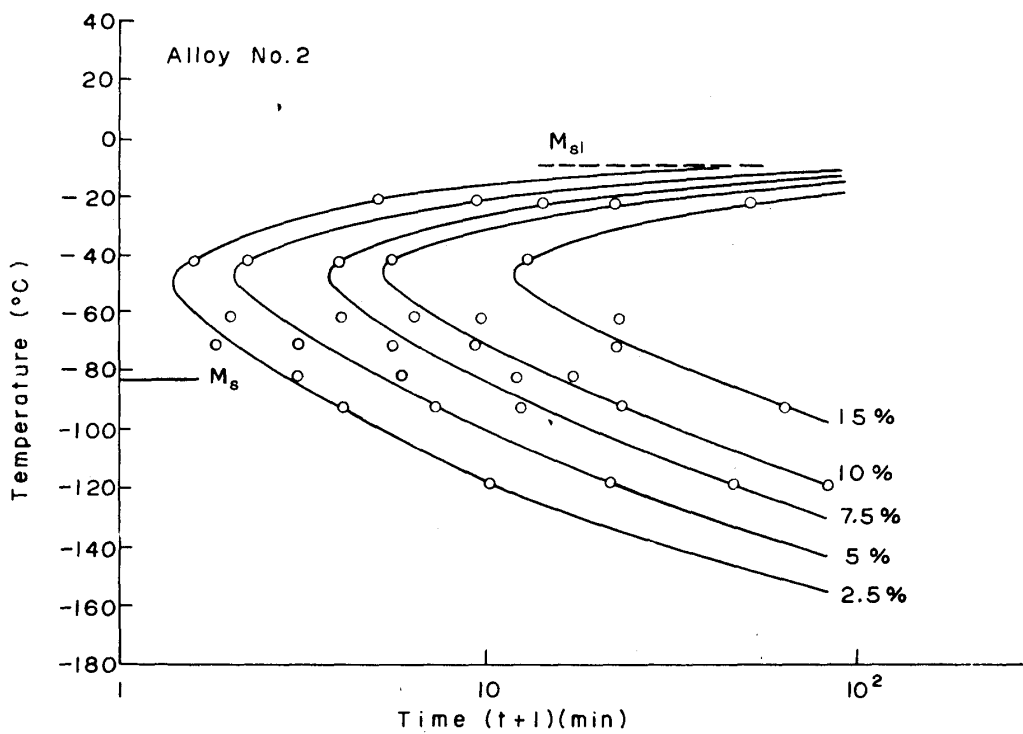Fig. 2.   T.T.T. curves for alloy No. 1 in the temperature range of martensite transformation.

Fig. 3.   T.T.T. curves for alloy No. 2 in the temperature range of martensite transformation.

a nose at -80°C. Figs. 3 and 4 show diagrams of the isothermal martensite trans-
formation for alloys No. 2 and 3, respectively, obtained by the same method. These
curves are also of C-type as in alloy No. 1. In the present work, the measurement for
alloy No. 3 in the temperature range of -100° to -196°C was not made. Later, an
interesting phenomenon was found in this temperature range, which will be reported
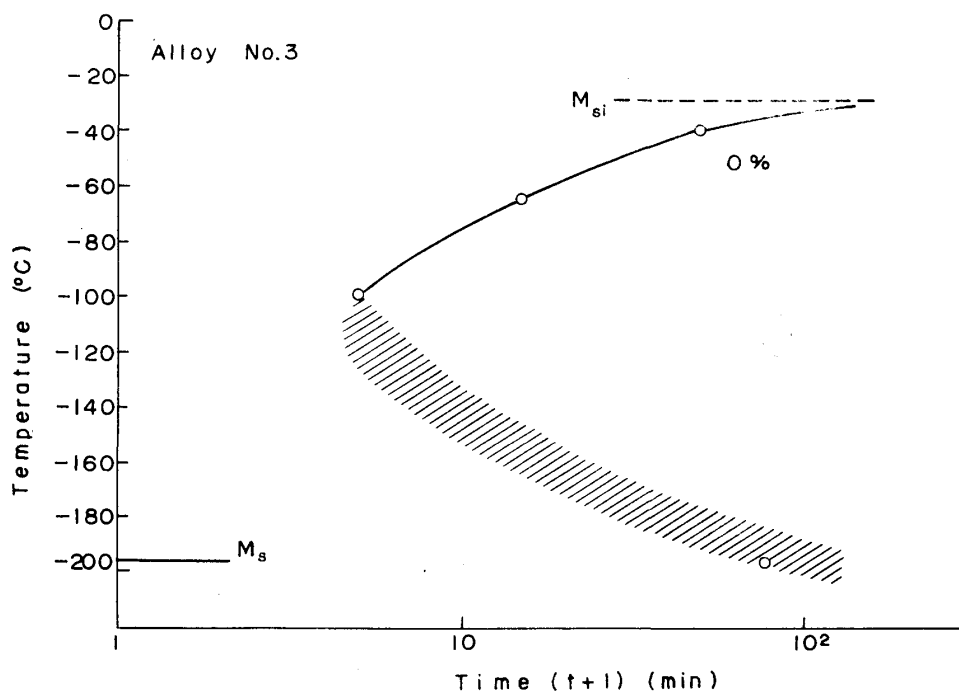in the succeeding paper.

Fig. 4. T.T.T. curve for alloy No. 3 in the temperature range of martensite transformation.

$\Delta F^{\alpha'\to\gamma}$ vs. T curves for Fe-Ni-17%Cr alloys are plotted in Fig. 5. The M_s
point in the figure was determined as follows: the M_s points were arranged not only
of the specimens used in the present work but also of those with various composi-
tions of similar alloys, determined by other workers. Fig. 6 shows the M_s points
thus determined, and a chain line was drawn as the mean of values taken up for the
M_s point in Fig. 5. The M_{si} point in Fig. 5 is the highest temperature at which the
isothermal martensite transformation occurs, as shown in Figs. 2 to 4. T_{max} is the
temperature at which the rate of transformation is maximum, namely, the tem-
perature of the nose. T_0, the temperature at which $\Delta F^{\alpha'\rightleftharpoons\gamma}=0$, can be determined
by the intersection of dotted lines and the straight line of $\Delta F^{\alpha'\rightleftharpoons\gamma}=0$ in Fig. 5. Fig.
7 shows the temperatures of T_0, M_s, M_{si} and T_{max} as the function of Ni content in
alloys with 17~18%Cr. In the figure, it is seen that M_s and T_0 lower in parallel, as
Ni content increases to about 6%, beyond which the M_s point lowers markedly,
while T_0 slowly. It is noticeable that in these alloys the degree of supercooling is
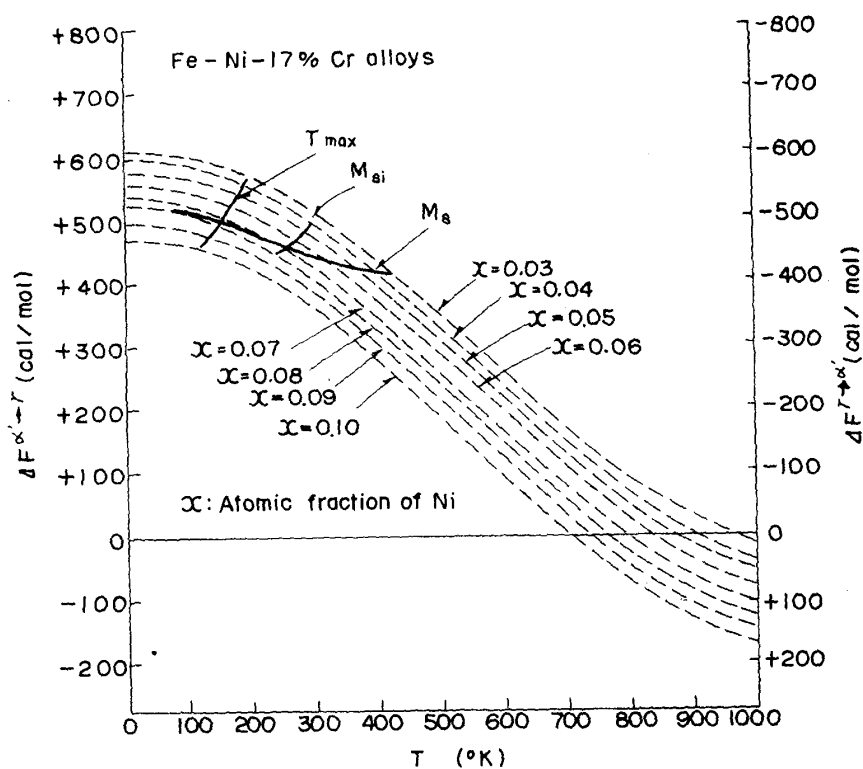very large; that is, these alloys can be supercooled as far as 500° to 800°C with

Fig. 5. Change of free energy accompanying the martensite transformation in Fe-Ni-17% Cr alloys.
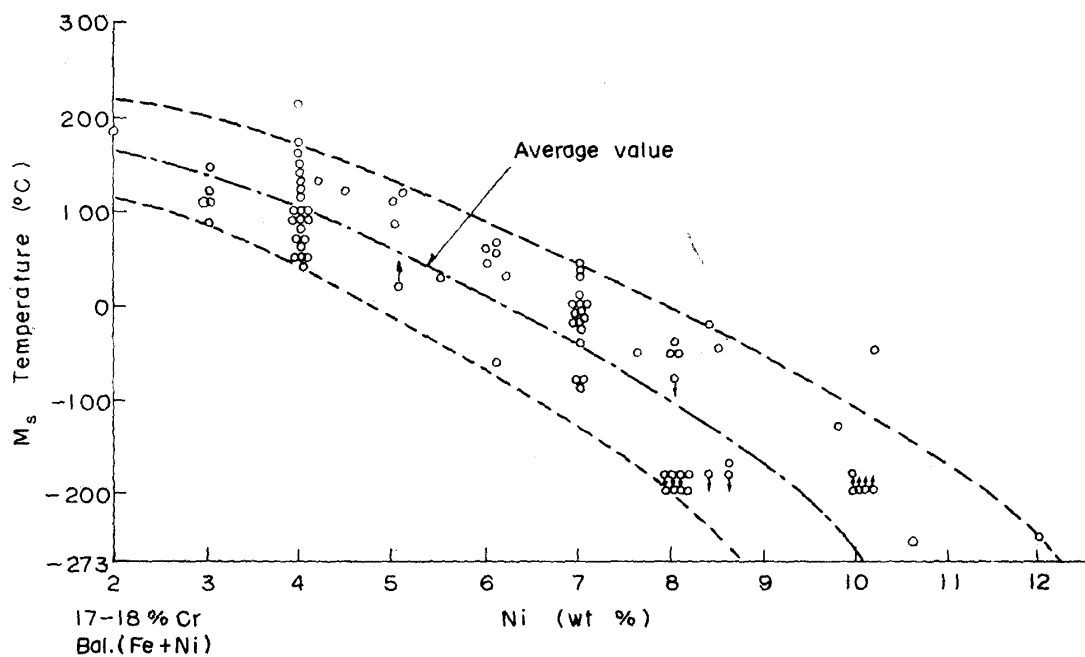

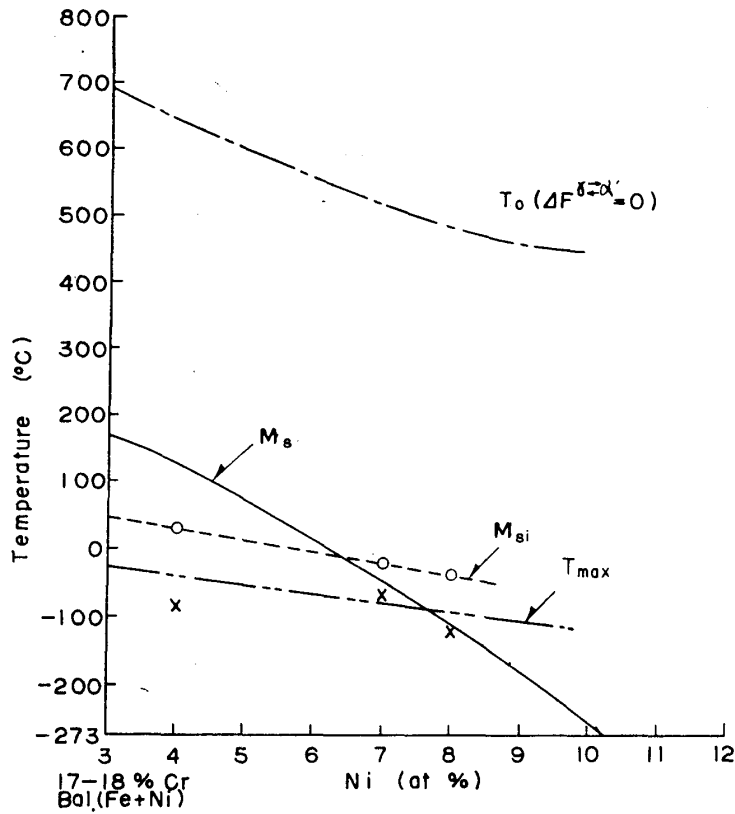Fig. 6. Effect of Ni content on the M_s point of Fe-Ni-Cr alloys.

Fig. 7. T_0, M_s, M_{si} and T_{max} vs. Ni content for Fe-Ni-Cr alloys.
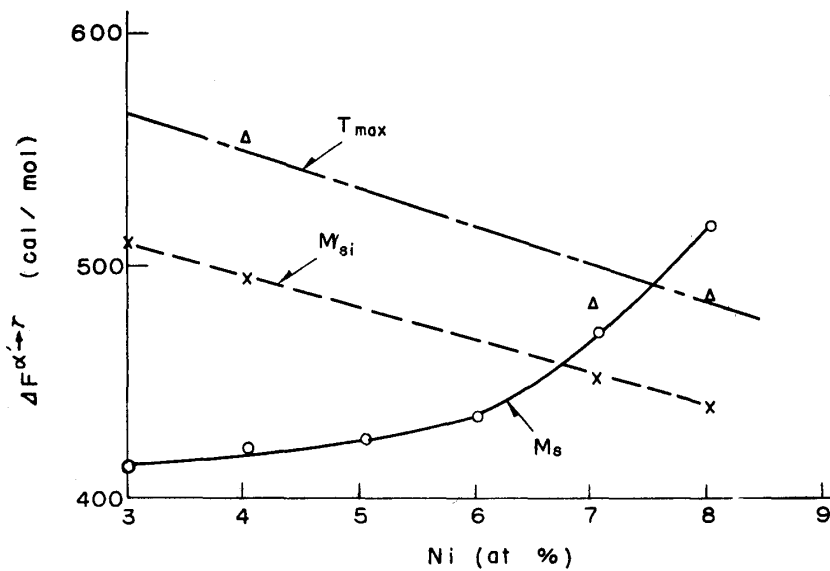

Fig. 8. Driving force necessary for martensite transformations at M_s, M_{si} and T_{max} points as a function of Ni content.

increasing Ni content, while in carbon steel it is only about 200°C. This indicates that a considerably large driving force is required in athermal martensite transformation. M_{si} point lowers with increasing Ni content, but it is not so pronounced

as M_s point, and when Ni content exceeds about 7%, the M_{si} point becomes higher than M_s; that is, when Ni content exceeds 7 % the isothermal martensite transformation takes place before the athermal martensite transformation occurs on cooling. A similar relation is seen in M_s and T_{max} points, T_{max} being higher than that of M_s, when Ni content exceeds 7.5 %. Fig. 8 shows the relations between $\Delta F^{\alpha' \to \gamma}$ at M_s, M_{si} and T_{max} points and Ni content. The driving force at M_s point increases from 420 to 530 cal/mole as Ni content increases from 3 to 8%, and rapidly increases when Ni content exceeds 6%. It is also seen in Fig. 8 that the stored free energy at M_{si} point decreases, as the Ni content increases, while that at M_s point increases and is less than that of M_s when Ni content exceeds about 7%. Similarly, the stored free energy at T_{max} points decrease as the Ni content increases.

2. Fe-Ni-Mn alloys

In order to see whether the above-mentioned results were applied to other alloys, similar experiments were carried out with Fe-Ni-Mn alloys.

The free energy for Fe-Ni-Mn alloys has not yet been calculated. So, the energy for Fe-Mn alloys was first calculated by a method similar to that of Kaufman and Cohen[5]. The result is as follows:

$$\Delta F^{\alpha' \to \gamma} = (1 - z)\,(1202 - 2.63 \times 10^{-3}\,T^{-2} + 1.54 \times 10^{-6}\,T^3)$$
$$+ z\,(- 2390 - 2.723\,T + 2.893 \times 10^{-6}\,T^3) + z\,(1 - z)$$
$$\times\,[- 889 - 0.192\,T\,(1 - l\,n\,T)]\ \text{cal/mole}\,, \tag{2}$$

where z is atomic fraction of Mn. Fig. 9 shows the change in free energy calculated by Eq. (2) when the content of Mn changed from 0 to 15 atomic %. In the figure, M_s and A_s ($\alpha' \to \gamma$) points by Hansen[6] were also shown. Fig. 10 shows the phase boundaries of $\alpha/\alpha+\gamma$ and $\alpha+\gamma/\gamma$ in equilibrium diagram of Fe-Mn, and also shows M_s and A_s curves, and T_0 introduced from Fig. 9. The relation $T_0 = 1/2\,(M_s + A_s)$ almost holds in the Fe-Mn system as seen in other martensite transformations.

From Eq. (2) and the change in free energy accompanying the martensite transformation in the Fe-Ni system[5], the free energy in Fe-Ni-Mn alloys can be calculated as follows:

$$\Delta F^{\alpha' \to \gamma} = (1 - x - z)\,(1202 - 2.63 \times 10^{-3}\,T^2 + 1.54 \times 10^{-6}\,T^3)$$
$$+ z\,(- 2390 - 2.723\,T + 2.893 \times 10^{-6}\,T^3) + x\,(- 3700 + 7.09$$
$$\times\,10^{-4}\,T^2 + 3.91 \times 10^{-7}\,T^3) + z\,(1 - x - z)\,[- 889 - 0.192\,T$$
$$\times\,(1 - l\,n\,T)] + x\,(1 - x - z)\,[3600 + 0.58\,T\,(1 - l\,n\,T)]\ \text{cal/mole}\,, \tag{3}$$

where x and z are the atomic fraction of Ni and Mn, respectively.

(5) L. Kaufman and M. Cohen, Trans. AIME, **206** (1956), 1393.

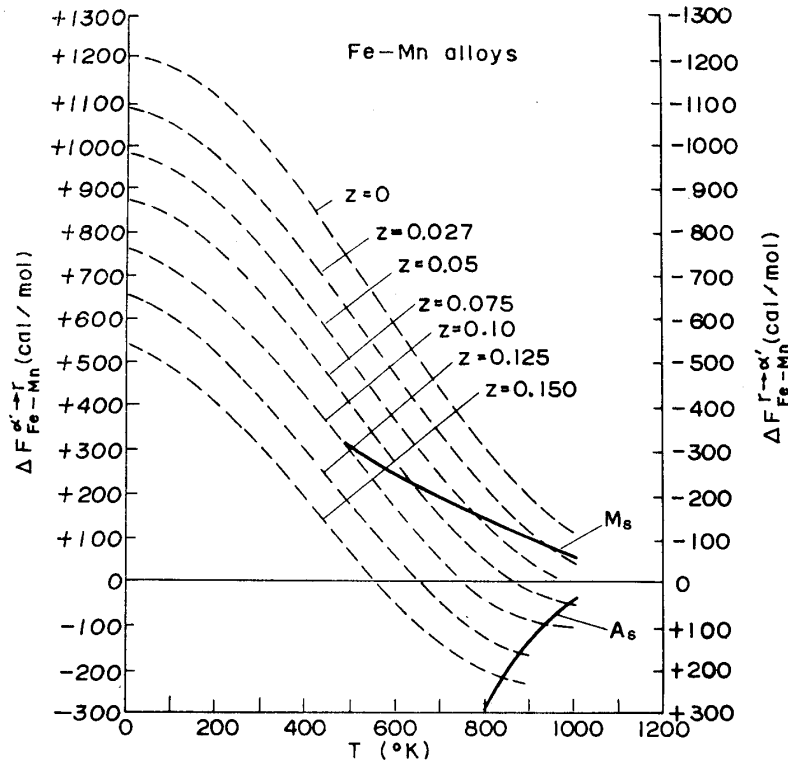(6) H. Hansen, *Constitution of Binary Alloys*, (1958), 664.

Fig. 9. Free energy change accompanying the martensite transformation in Fe-Mn alloys.   z: Atomic fraction of Mn.
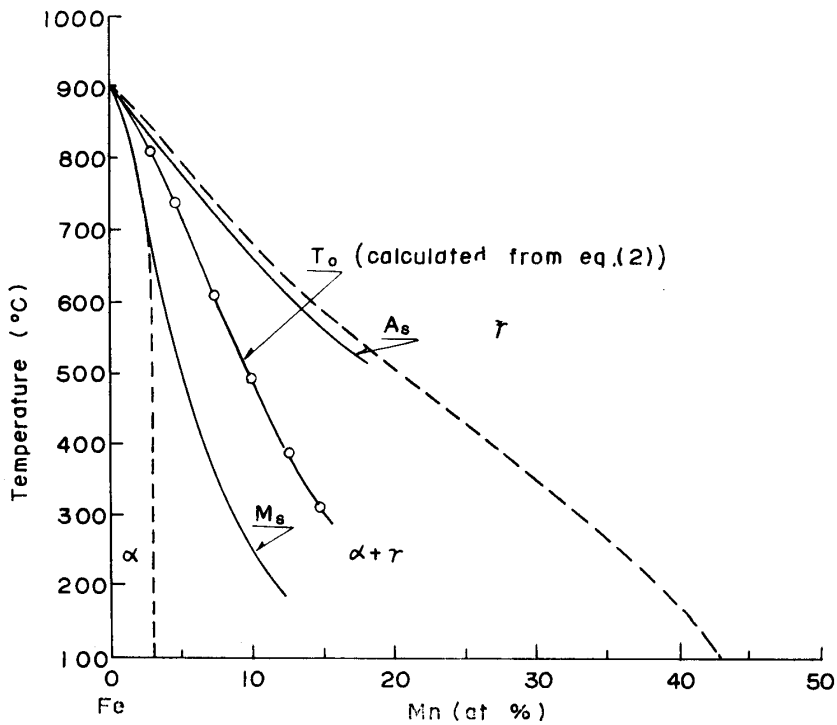

Fig. 10. The $\alpha/\alpha+\gamma$ and $\alpha+\gamma/\gamma$ phase boundaries (dotted lines), M_s, A_s, and T_0 points in Fe-Mn alloys. The solid lines show M_s, A_s and T_0 temperatures.
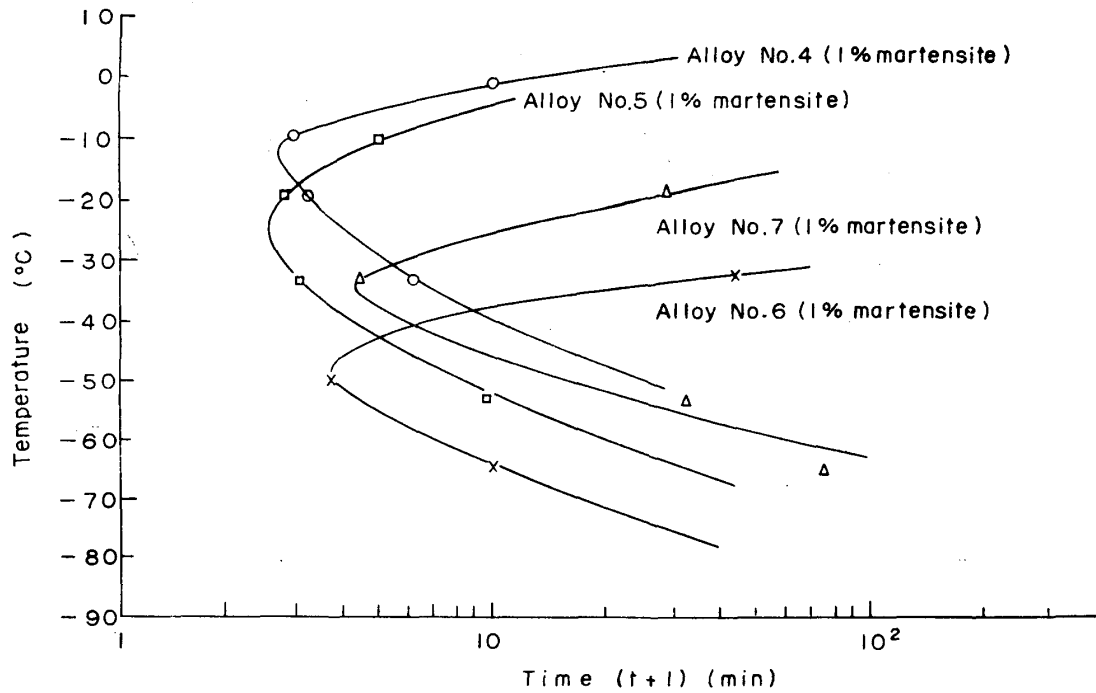
Fig. 11.   T.T.T. curves for isothermal martensite transformation in Fe-Ni-Mn alloys.
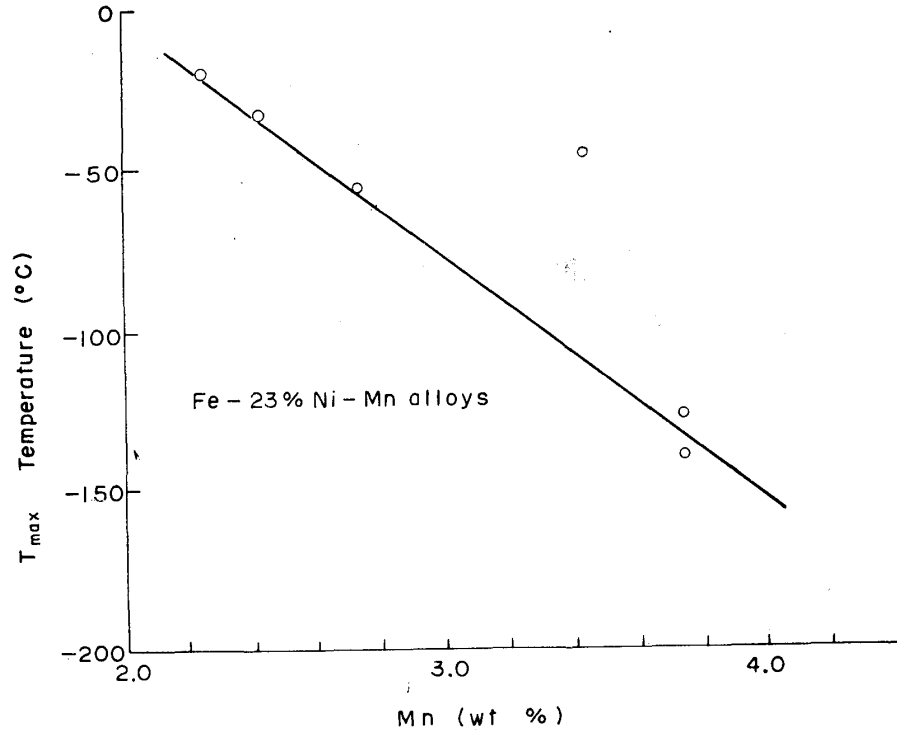

Fig. 12.   Temperature (T_{max}) of maximum rate of isothermal martensite transformation in Fe-Ni-Mn alloys.

Fig. 11 shows T.T.T. curves for the isothermal martensite transformations of Fe-Ni-Mn alloys. C-type curves are seen also in this case as those in Fe-Ni-Cr alloys. It should be noted in Fig. 11 that T_{max} point showing the temperatures of the nose lowers, except that for the alloy No. 7, as Mn content increases. This is observed also in Fig. 7 when the Ni content increases in Fe-Ni-Cr alloys. Fig. 12 shows the relation between T_{max} and Mn content, the results of other workers[2][7][8] being taken into account, in which it is seen that T_{max} lowers linearly with the increase in Mn content. This relation was first pointed out by Shih, Averbach and Cohen[7]; according to the above result, however, T_{max} does not lower so rapidly as pointed out by them.
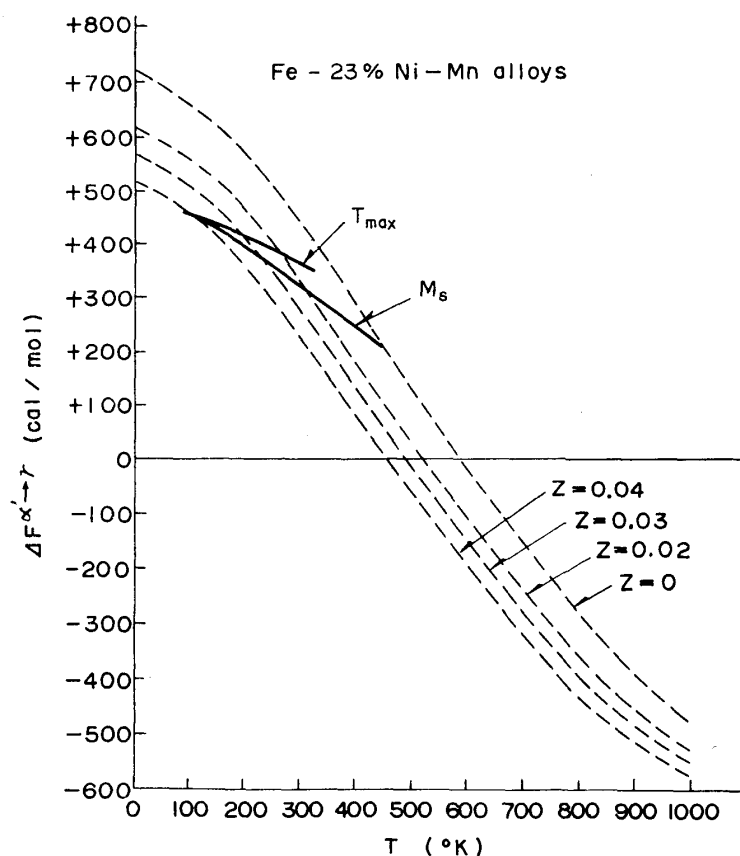

Fig. 13. Change of free energy accompanying the martensite transformation in Fe-Ni-Mn alloys.   z: Atomic fraction of Mn.

Fig. 13 shows the change in free energy calculated by Eq. (3) when the Mn content increases from 0 to 4 % in alloys with a constant content of Ni (23%), together with M_s and T_{max}. Fig. 14 shows the change of temperatures M_s, T_{max}, A_s and T_0 as the Mn content increases. As seen in this figure, the relation $T_0 = 1/2\,(M_s + A_s)$ nearly holds, though the curve T_0 is somewhat closer to M_s than to A_s. Curves M_s and T_{max} intersect at about 3.5% Mn, beyond which T_{max} point becomes higher than

(7) C.H. Shih, B.L. Averbach and M. Cohen, Trans. AIME, **203** (1955), 183.

(8) R.E. Cech and J.H. Hollomon, Trans. AIME, **197** (1953), 685.

that of M_s as Mn content increases, that is, the isothermal martensite transformation occurs at a temperature above M_s. A similar phenomenon is also seen in Fe-Ni-Cr alloys, in which the relation between M_s and T_{max} becomes reverse when the Ni
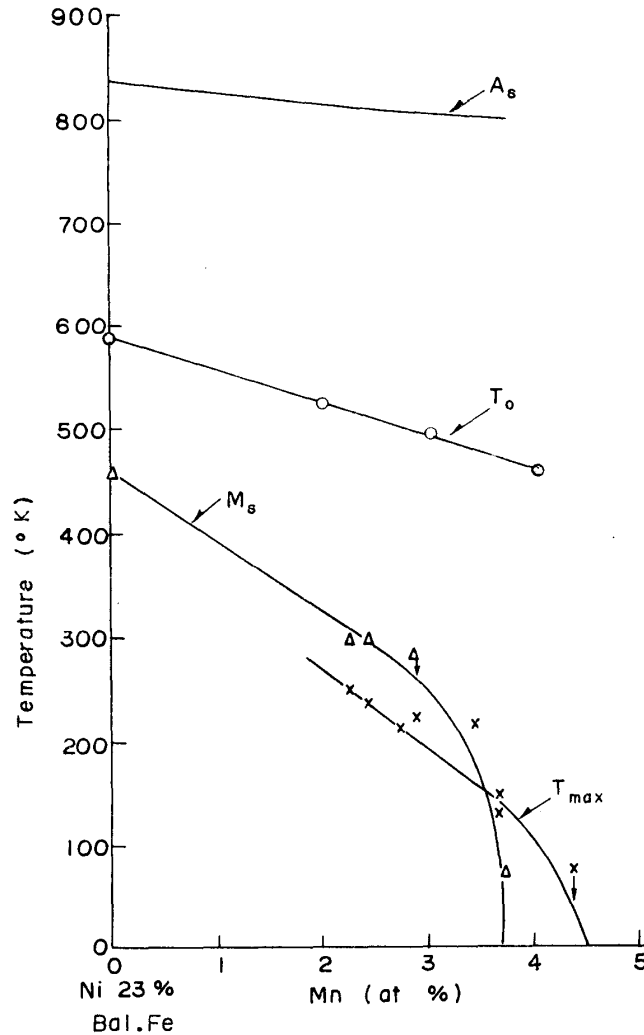

Fig. 14. A_s, T_0, M_s and T_{max} temperatures vs. Mn content in Fe-Ni-Mn alloys.

content increases to 7.5%, as seen in Fig. 7.   Fig. 15 shows the stored free energy at M_s and T_{max} points determined from Fig. 13 as a function of the Mn content. When the Mn content is less than about 3.5%, the free energy at T_{max} point is larger than that at M_s point, but the relation between these two becomes inverse beyond this content.   As in Fe-Ni-Cr alloys, it can be seen from the change in free energy that there exists a composition beyond which the isothermal martensite takes place more easily than the athermal martensite in Fe-Ni-Mn alloys.   The free energies at M_s and T_{max} points become equal to each other, at about 430 cal/mole, which coincides nearly to 490 cal/mole of Fe-Ni-Cr alloys.
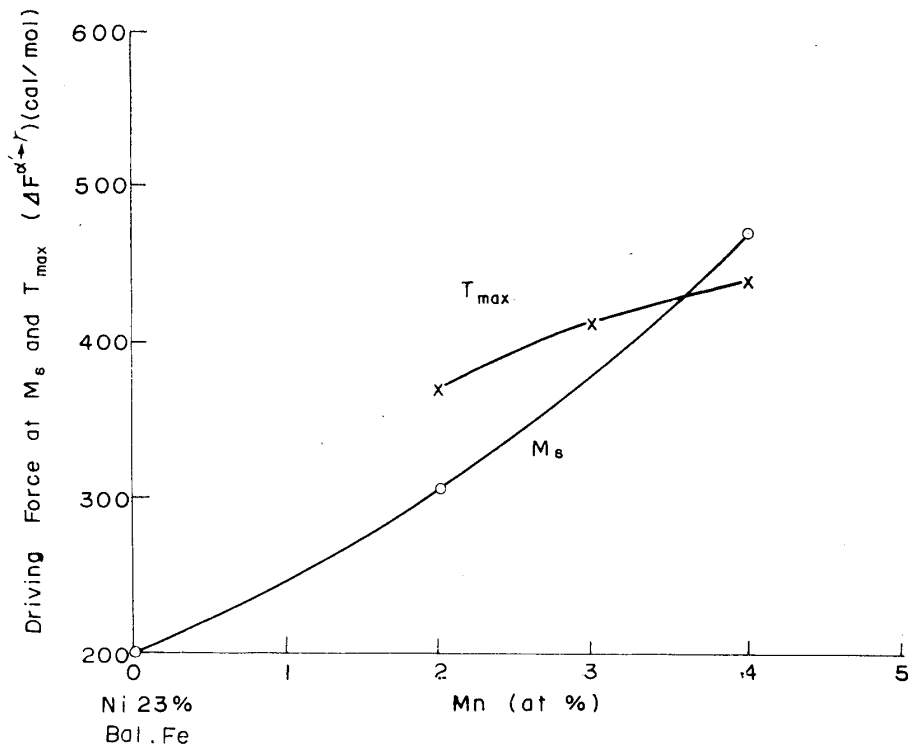
Fig. 15.   Driving force necessary for martensite transformations in Fe-Ni-Mn alloys as a function of Mn content.

IV.   Discussion

The thermodynamic treatments of the relations between the athermal and the isothermal martensites in Fe-Ni-Cr and Fe-Ni-Mn alloys led to similar results.   It is supposed from these results that the phenomena mentioned in the preceding sections are common characteristic existing not only in alloys of these two systems but also in other alloys in which the isothermal martensite transformation occurs. One of characteristics is that the isothermal martensite transformation occurs when the driving force at M_s, that is, the driving force necessary to begin the athermal martensite transformation attains to a large amount.   This is suggestive of an idea that it attains to the formation of the critical nucleus of isothermal martensite by the effect of thermal fluctuation, though the free energy sufficient to start the athermal martensite transformation cannot be acquired by supercooling alone.   It is possible that the nuclei of the athermal martensite may be formed by supercooling, but in order to form the nuclei of the isothermal martensite, the nucleus-forming atom should be displaced within a small region, since the forming is not sufficient by supercooling alone.   According to such a consideration, the fact can well be explained that the isothermal martensite transformation proceeds in a constant temperature.   When the critical nuclei are formed, the transformation will be propagated by the same mechanism as in the athermal martensite, as seen in the results of other workers[7][9].

(9)   J. Philibert and C. Crussard, J. Iron and Steel Inst., **180** (1955), 39.

When Ni or Mn contained in the Fe-Ni-Cr or in the Fe-Ni-Mn alloys exceeds a certain amount, respectively, the isothermal martensite transformation takes place before the athermal transformation on cooling, the stored free energy for the isothermal martensite being $430 \sim 490$ cal/mole. This gives an interesting suggestion on the martensite transformation, but a further consideration on this problem will not be taken owing to the essential limitation of thermodynamics.