The Ms-Temperature and Martensite Structure of Fe-C Alloys Containing Mn, Si, or Cr under High Pressure*

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The effects of Mn, Si or on the Ms-temperature and the martensite structure of Fe-0.3%C alloy were examined under hydrostatic pressure up to 41kbar using a "girdle" type apparatus. The results obtained are as follows ;

The Ms-temperature was lowered approximately 40°C/10kbar in all alloys and its tendency was not significantly affected by alloying elements. The measured Ms-temperatures at 1 atm (0.001kbar), 29 and 38.5kbar are in reasonable agreement with those calculated by Predmore's equation concerning the free energy change for $\gamma \rightarrow \alpha'$ transformation. The plate-like structure was observed as a result of the martensite transformation above 38.5 kbar. The reason for the appearance of this structure can be explained qualitatively by P-T diagram of iron. The hardness of martensitic structures increases with an increase of pressure. This tendency can be interpreted by the change of in the martensite structures, resulting from the fact that the Ms temperature is lowered by pressure.

1. Introduction

It is well known that the $\alpha \rightarrow \varepsilon'$ transformation was induced by pressurizing to more than 130kbar in pure iron[1][2] and also ε phase was observed in some alloys such as Fe-Mn[3] and Fe-Ni-Cr[4] alloys even at atmospheric pressure. Therefore, it is expected that by the increase of pressure and the addition of alloying elements, the process of martensitic $\gamma \rightarrow \alpha'$ transformation and the martensite structure obtained is affected by the easy formation of ε phase.

On the other hand, the change of Ms-temperature was examined in the Fe-C,[5][6] Fe-Ni,[5]~[7] Fe-Cr,[5][8] Fe-Mn[9] alloys and the low alloy steels[10][11] under high pressure and it was reported that Ms-temperature for $\gamma \rightarrow \alpha'$ transformation is depressed by pressurizing. The depressions of Ms-temperature by pressurizing were in agreement with those calculated on the basis of the free energy changes for martensite transformation given by the following relationship

$$\Delta G^{\gamma \rightarrow \alpha'}(x, T, P) = \Delta G_o^{\gamma \rightarrow \alpha'}(x, T) + 23.9 \times \int_0^P \Delta V^{\gamma \rightarrow \alpha'}(x, T)dP \quad (1)$$

where $\Delta G^{\gamma \rightarrow \alpha'}(x, T, P)$ and $\Delta G^{\gamma \rightarrow \alpha'}(x, T)$ are the changes in free energy for the transformation at an applied hydrostatic pressure of P kbar and at atmospheric pressure respectively for an alloy containing x atomic fraction of alloying elements, and $\Delta V^{\gamma \rightarrow \alpha'}(x, T)$ is the change in the molar volume. The equation (1) means that the transformation behaviour caused by pressure is strongly affected by its volume change.

The effect of some elements on the isothermal transformation of Fe-C alloys under high pressure was already examined by the present authors.[12][13] From the results, it was pointed out that the change of the structure in the alloys under high pressure was related to the volume change in $\gamma \rightleftarrows \alpha + Fe_3 C$ transformation with the addition of alloying element as reported by Kenneford.[14] Therefore, if the volume change with martensite transformation is affected by addition of alloying element, the pressure dependence of the Ms-temperature in alloys should be different from that in the Fe-C alloy.

The purpose of the present investigation is to examine the effects of Mn, Si or Cr on the martensitic transformation behaviour in Fe-C alloy containing carbon of about 0.3% under hydrostatic pressure up to 4 lkbar. A special emphasis is placed on the determination of the Ms-temperature and on the observation of the structural changes of martensite caused by pressure and addition of alloying elements.

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2. Experimentals

2.1. Materials

The materials used in this work were high purity iron-carbon alloys containing about 0.3%C, to which Mn, Si and Cr were added separately in three level up to 1.5%. These materials are similar to those used for the investigation[13] of the isothermal transformation under high pressure. The chemical composition is shown in **Table 1.**

Table 1. Chemical composition of specimens.

	C	Si	Mn	P	S	Cr
A-2	0.28	0.001	0.004	0.001	0.002	—
A-4	0.42	0.001	0.001	0.001	0.003	—
C-1	0.35	0.010	0.003	0.001	0.004	0.54
C-2	0.38	0.009	0.001	0.001	0.005	1.06
C-3	0.37	0.008	0.002	0.001	0.006	1.60
M-1	0.26	0.004	0.32	tr	0.005	—
M-2	0.26	0.001	0.59	tr	0.005	—
M-3	6.23	0.001	1.37	tr	0.005	—
S-1	0.30	0.58	0.02	0.001	0.004	—
S-2	0.30	0.98	0.02	0.001	0.004	—
S-3	0.35	1.51	0.005	0.001	0.004	—

The alloying elements as described above were chosen from the following reason: these lower the stacking fault energy so that the ε phase is easily formed. At atmospheric pressure, ε phase was observed in the Fe-Mn alloys[10][15] containing Mn of more than 10% and in the Fe-4.2%C-1.5%Si alloy[16] quenched from the liquid state by splat cooling. It is supposed that martensite structure in the Fe-Cr alloy under high pressure was formed by $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ transformation.[8] Consequently, the addition Mn, Si and Cr is expected to lower the transition pressure for $\alpha \rightarrow \varepsilon'$ transformation in Fe-C alloys. As described already, if the volume change on the formation of martensite is affected by the alloying element, the pressure dependence of Ms-temperature in alloys is expected to be different from that in Fe-C alloys. Kenneford[14] examined the effect of some elements on the volume change for $\gamma \leftrightarrows \alpha +$ Fe$_3$C transformation at Ac$_3$ temperature and reported that Si had the most reducing effect on its volume change, Cr had a strongly adverse effect and Mn had a slightly increasing effect on the volume. Kenneford reported that the volume change for $\gamma \leftrightarrows \alpha +$ Fe$_3$C transformation relates

to the susceptibility of steel to cracking on quenching which will be related to the volume change in martensite transformation.[14] Consequently, the volume change for $\gamma \leftrightarrows \alpha +$ Fe$_3$C has an important meaning on the consideration of the effect on the Ms-temperature under high pressure.

On the other hand, as Ms-temperature is lowered by increasing the amount of alloying elements, it becomes difficult to measure the Ms-temperature of such alloys under high pressure. So, the maximam amount of alloying element in these materials was limited to 1.5%.

2.2. Measurement of Ms-temperature

The Ms-temperature at atmospheric pressure was determined using the cooling curve of the specimen with 3mm in diameter and 1mm thickness, austenitized at 900°C for 10min and then quenched by blowing argon gas. The cooling rate was attained to about 1000°C/sec at the vicinity of Ms-temperature.

Ms-temperature under high pressure was measured by the method of Greninger and Troiano that was also used by Radcriffe et al.[6] At first, two specimens with 3mm in diameter and 3 mm long were pressurized to a given pressure by the method which was described in details in the previous papers.[13][17] Then, the specimens were austenitized at 950°C for 15min and quenched to the desired temperatures at which the martensitic transformation is expected to occur, and held for 2~3 sec. Then, the specimens were reheated to 300°C and held for 2min. Finally, the specimens were quenched to room temperature and the pressure was released. Consequently, all of the martensite formed on the first quenching was revealed as a dark-etched structure readily distinguishable from the martensite formed on the second quenching and during the release of pressure. It was reported[18] that the structure obtained by this method was changed by tempering temperature and holding time and it became difficult to distinguirh metallographically between martensite formed on the first quenching and the other structure, which was formed after the quenching. But, the conditions in this experiment were sufficient to temper any martensite formed without any further transformation of austenite.[12][13]

3. Results

3.1. Ms-temperature

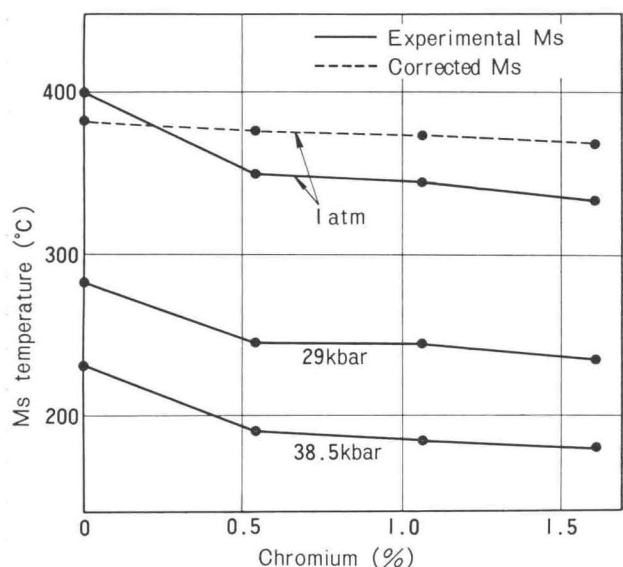Some results on Ms-temperatures measured at 1 atm,

Fig. 1. The Ms temperature in Fe-C-Cr alloys under various pressures. The broken line shows the Ms of Fe-C-Cr alloys at latm corrected at the carbon level of 0.3%C by the Steven's equation[19].

29 and 38.5 kbar are shown in **Fig. 1** and **Fig. 2**. **Fig. 1** shows the change of Ms-temperature by the addition of Cr under various pressure. As the content of carbon in Fe-C-Cr alloys used in this experiment was slightly fluctuated, the Ms-temperatures of those alloys measured at latm were corrected at the carbon level of 0.3%C by Steven's equation[19] and the results were indicated by a broken line in this figure. It is shown in this diagram that the lowering of Ms-temperature with the increase of Cr is essentially the same for various pressures. The pressure dependence of Ms-temperature in the alloys which contain the maximum amount of alloying elements in this
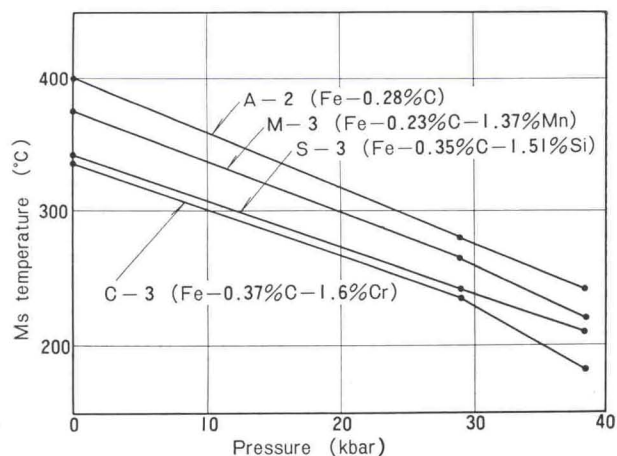
experiment is shown in **Fig. 2**. It is shown that the Ms-temperatures are lowered approximately 40°C/10kbar in all alloys. It is possible to consider from the results shown in **Fig. 1** and **Fig. 2** that the pressure dependence of Ms-temperature is unaffected by the kind and amount of alloying element.

The results of Ms-temperature measured under various pressures and those calculated by Predmore's equation[10]* concerning the free energy change for $\gamma \rightarrow \alpha'$ transformation are shown in **Table 2**. The calculated Ms-tempera-

* See appendix

Table 2. Comparison of calculated and experimental Ms-temperatures (°C) under various perssures.

	1 atm		29 kbar		38.5kbar	
	cal	exp	cal	exp	cal	exp
A-2	430	400	320	280	280	240
A-4	375	340	270	240	230	210
C-1	395	350	295	245	255	190
C-2	390	340	270	245	230	185
C-3	380	335	260	235	230	180
M-1	430	400	330	290	295	240
M-3	425	385	325	275	290	235
M-3	405	375	305	265	270	220
S-1	425	360	325	275	290	230
S-2	425	360	325	275	290	220
S-3	375	340	270	240	230	210

cal=calculated by Predmore's equation[10], exp=experimental

Pressur / Sample	l atm	29kbar	38.5kbar	41kbar
A − 2	P	P	P+E	P+E+L
A − 4	P+L	P+L	L+E	L+E
M − 3	P	P	E	E
S − 3	P+L	P+L	L+E	L+E
C − 3	P+L	P+L	L+E	E

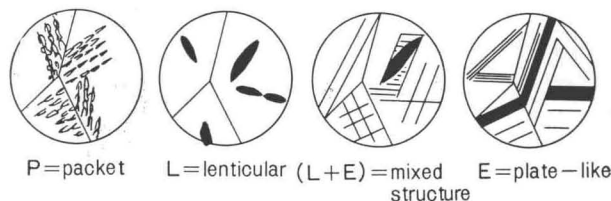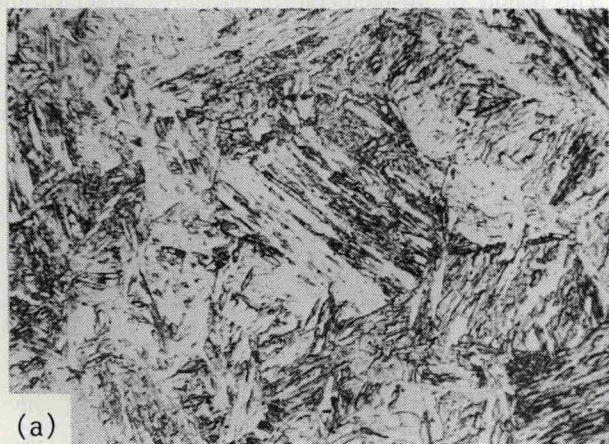P=packet   L=lenticular   (L+E)=mixed structure   E=plate−like

Fig. 3. Effect of pressure on free energy curve ($\Delta G^{\alpha' \rightarrow \gamma}_{(x, T, P)}$) of Fe-0.42%C alloy (A-4). Experimental Ms points were also plotted.

Fig. 2. Effect of pressure on Ms temperature for various Fe-C base alloys.

ture was determined on the basis of the thermodynamic consideration proposed by Kaufman et al.[20] Namely, Ms-temperature is defined as the one at which the difference in the free energy between γ and α phases is equal to the value of the driving force required for the initiation of the martensite transformation. Therefore, when the spe-

(a)

(b)

(c) $\vdash\!\!-\!\!-\!\!\dashv$ 30μ

Photo. 1. Effect of pressure on martensite structure in Fe-0.26%Mn alloy (M-2).
    (a) 1atm   (b) 29kbar   (c) 38.5kbar

cimen is cooled to a temperature at which the equation (2) is satisfied, the martensitic transformation occur first.

$$\Delta G^{\gamma\to\alpha'}(x, T, P) + \Delta G_v^{\gamma\to\alpha'} \leqq 0 \tag{2}$$

Here the value of driving force of 300cal/mol was used in this calculation. It is thought that this is a reasonable value, comparing with the value of 302cal/mol for the low alloy steels[10] and 290cal/mol for iron-carbon alloys obtained[6)21)] thermodynamically. As an example of this calculation, the relationship between the change of the free energy with temperature and the measured Ms-temperature of Fe-0.42%C (A-4) is shown in **Fig. 3.** It can be seen in this figure that the driving force is about 300 cal/mol. Although the difference ranging from 30 to 60°C is recognized between measured and calculated Ms-temperature in the **Table 2,** the change of Ms-temperature by pressure can be predicted qualitatively from the calculation as described above.
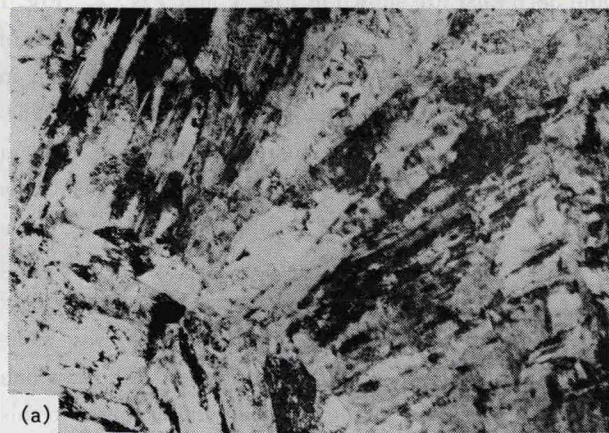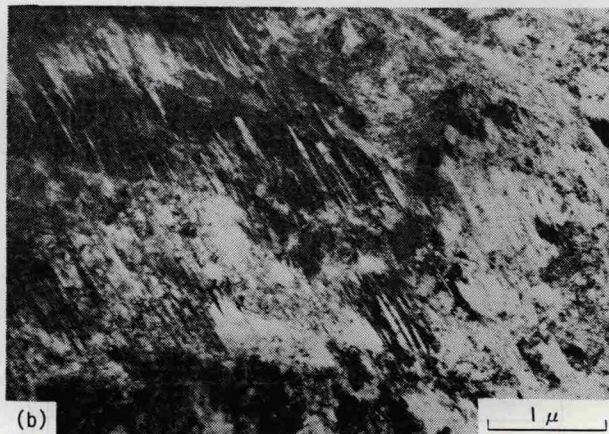

(a)

(b) $\vdash\!\!-\!\!\dashv$ 1μ

Photo. 2. Transmission electron micrographs of Fe-0.35%C-1.51%Si alloy (S-3).
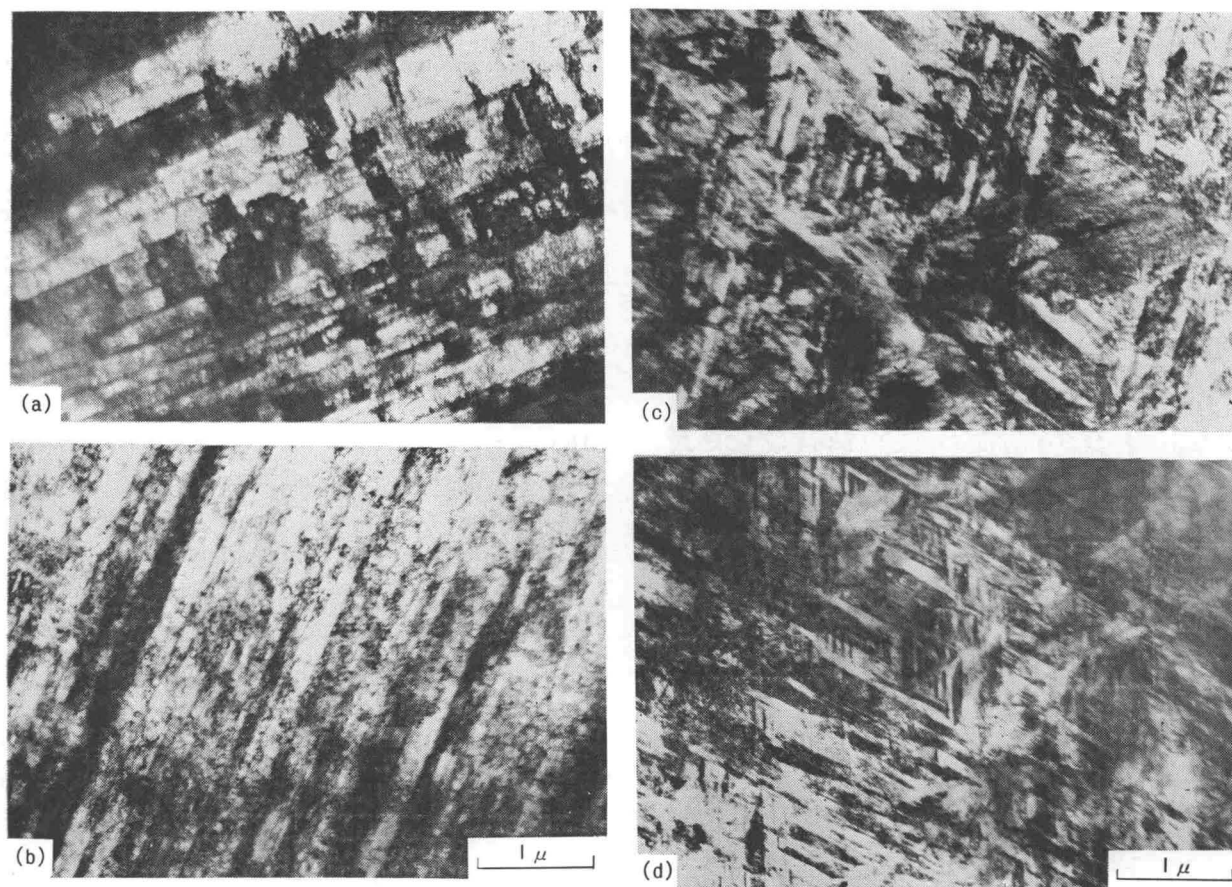   (a) Lath martensite, 1atm   (b) Internally twinned martensite, 29kbar

Photo. 3. Transmission electron micrographs of plate-like martensite in Fe-0. 23%C-1. 37%Mn alloy (M-3) quenched to 200°C and tempered at 300°C for 2min at 38. 5kbar.
(a) and (b) Tempered region (c) and (d) Martensite formed from untransformed austenite.

3. 2. Martensite structure

The optical micrographs of martensite structure in the alloys, containing carbon less than 0. 3%, quenched from austenitized temperature under various pressures are shown in **Photo. 1.** The gradual change from packet structure (a) to plate-like one (b) by the increase of the pressure can be seen. On the other hand, in the alloys containing carbon more than 0. 3%, the mixed structure of packet and lenticular is shown at the atmospheric pressure and nearly the lenticular structure at 29kbar and further at 38. 5kbar the mixed structure of lenticular and plate-like is observed. The transmission electron microstructure of martensite changes from the lath to the twin type by pressrizing as shown in **Photo. 2.** This fact is in an agreement with the results reported by Vyhnal et al.[22] The plate-like structure observed with an optical microscope is similar to one which was already reported in Fe-Cr alloys[8] under high pressure and Fe-Mn alloy[23] at

atmospheric pressure, as shown in **Photo. 3.**

As it is very difficult to discuss in detail the change of the martensite structure obtained by quenching under high pressure, the change is mainly estimated from the tempered martensite, which is obtained by the same method as to measure Ms-temperature. The results are shown in **Photos. 4, 5, 6, 7** and **8. Photo. 4** shows the tempered structure of primary martensite in Fe-0. 28%C alloy (A-4) quenched to the vicinity of Ms-temperature. In this photograph, the change from packet structure to plate-like one can be observed with an increase of pressure, and at 41 kbar fully plate-like structure. **Photo. 5** shown the structural changes in Fe-0. 23%C-1. 37%Mn alloy (M-3) as well as those shown in **Photo. 4.** The observation, it shows that the pressure at which the plate-like structure appeared was lowered by the addition of Mn to approximately 36 kbar, which was lower than that in the Fe-0. 28% alloy, It is likely that decrease in this pressure relates to the
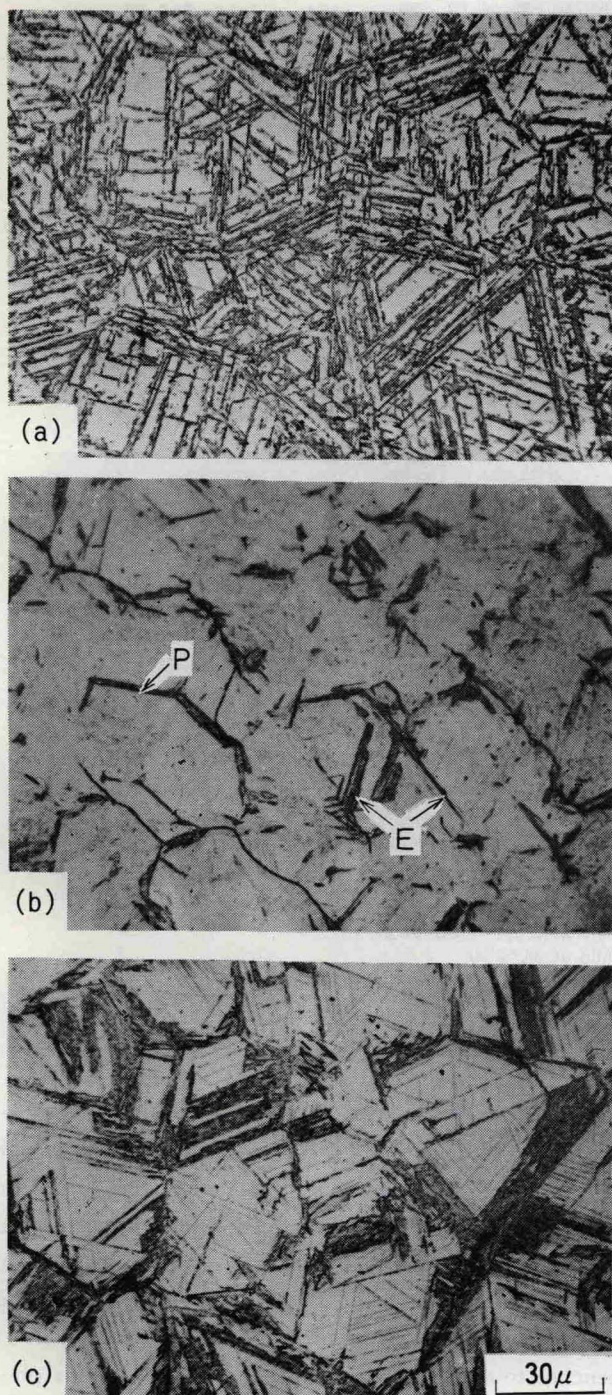
Photo. 4. Effect of pressure on martensite microstructure in Fe-0.28 %C alloy (A-2).
(a) Packet structure (P), quenched to 230°C at 29kbar.
(b) Packet (P) and plate-like (E) structures quenched to 220°C at 38.5 kbar.　　(c) Plate-llke structure (E), quenched to 180°C at 41kbar

lowering of the stacking fault energy and of the free energy of ε phase by the addition of Mn. Consequently, this fact is due to the depression of pressure at which the $\gamma \rightarrow \varepsilon'$ transformation occurs.

Photo. 6 shows the structural changes from packet to plate-like through the mixed structure of lenticular and plate-like martensites in Fe-0.37%C-1.60%Cr alloy (C-3). In the alloys containing carbon more than 0.3%, the plate-like structure is easy to distinguish metallographically from the other structure. The reason for this may relate to the difference in habit plane between structures observsd with change of carbon content.[24)25)] Therefore, as the difference in the growth direction or habit plane between plate-like and lenticular structures is observed as shown in **Photo. 7,** these structures are easily distinguishable. However, the distinction between the packet and plate-like structures was difficult, because they have the same habit plane.

Photo. 8 shows the change of martensite structure in Fe-0.42% and Fe-0.35%C-1.51%Si alloys, quenched to various temperatures below the Ms-temperature at 38.5 kbar. The plate-like structure is observed around the lenticular structure. It is also observed that the volume fraction of plate-like structure increases with the depression of the transformation temperature, but no change was observed on the volume fraction of the lenticular structure.

The martensite structures obtained in the alloys containing maximum amount of alloying element at high pressures are summarized in **Fig. 4.** The classification of martensite structure at latm in this figure was performed by observing the specimens water-quenched with an optical microscope and with a transmission electron microscope, because the Greninger-Troiano's method could not be applied at latm.

3.3. Hardness of martensite structure

The structural change of the martensite in a specimen with an increase of pressure occurs as described before. It is predicted that the mechanical property is influenced by the appearances of martensite structure. As the specimen size was not large enough to enable us to examine the various mechanical properties, only microhardness was measured on the specimens quenched under various pressures. **Fig. 5** shows the relationship between the microhardness and Ms-temperature, in low alloys. In this figure, it is indicated that with the depression of Ms-temperature or with an increase of pressure, the microhardness increases in all the alloys. The results are divided into two groups by carbon content in the alloys, which has a significant effect on the structural change of martensite
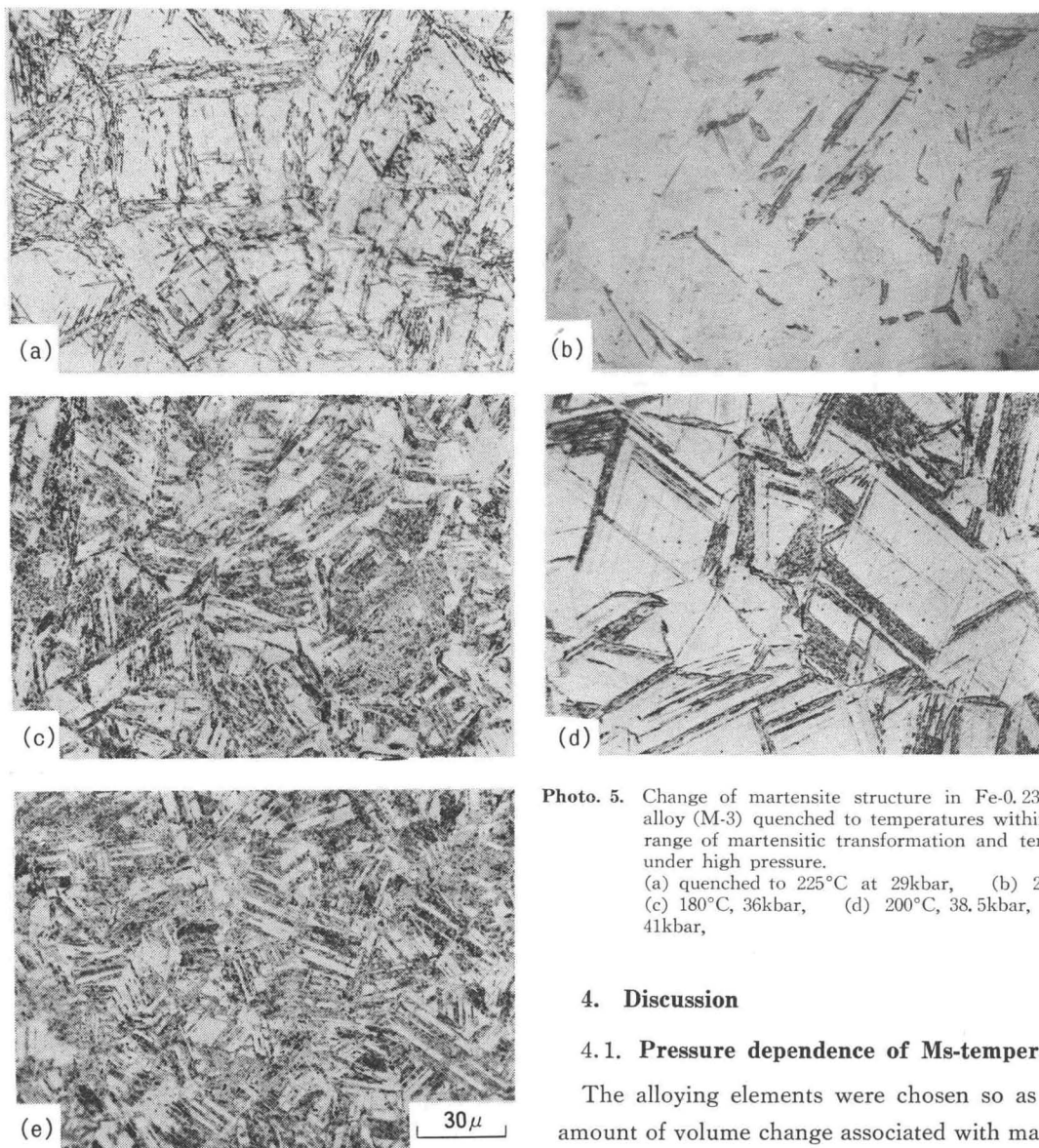
Photo. 5. Change of martensite structure in Fe-0. 23%C-1. 37%Mn alloy (M-3) quenched to temperatures within an expected range of martensitic transformation and tempered 300°C under high pressure.
(a) quenched to 225°C at 29kbar,   (b) 230°C, 33kbar, (c) 180°C, 36kbar,   (d) 200°C, 38.5kbar,   (e) 150°C, 41kbar,

4. Discussion

4.1. Pressure dependence of Ms-temperature

The alloying elements were chosen so as to vary the amount of volume change associated with martensite transformation on the basis of the results reported by Kenneford.[14] But, in spite of the difference in the kind or amount of the alloying element, the lowering tendency of the Ms-temperature was almost the same, that is approximately 40°C/10 kbar in all alloys. The reason can be considered as follows. As to be understood from the equation (1) and (2), the pressure dependency of Ms-temperature may be affected by the volume change in the formation of martensite. It is considered that this volume change will not only depend on transformation temperature but also on the kind and amount of alloying element.

Namely, this volume change increases with lowering of the temperature which is resulted from the defference in thermal-expansion-coeffcient between γ phase and marten-

under high pressure. Namely, when the pressure increases from 1 atm to 29 kbar, in the alloys containing carbon more than 0.3%, Ms-temperature above 350°C depresses to 280°C and also microhardness of approximately 530 HV increases to 700 HV, while no change of the hardness was observed by pressurizing to 38.5 kbar. On the other hand, with the depression of Ms-temperature, the microhardness increases about 25 HV per 10 kbar, in the alloys containing carbon less than 0.3%. Consequently, the depression of Ms-temperature with an increase of pressure is closely connected with the changes of the martensite structure followed by the increase of hardness.
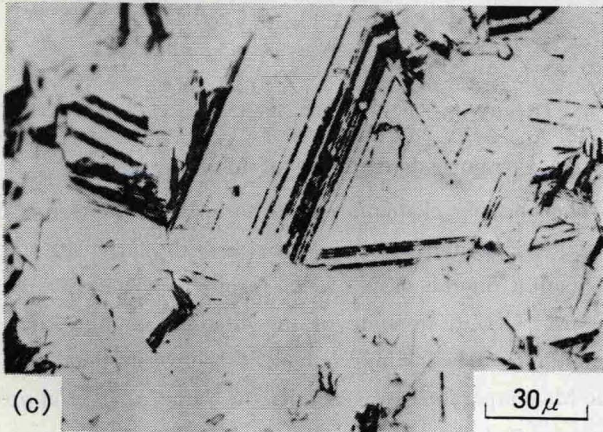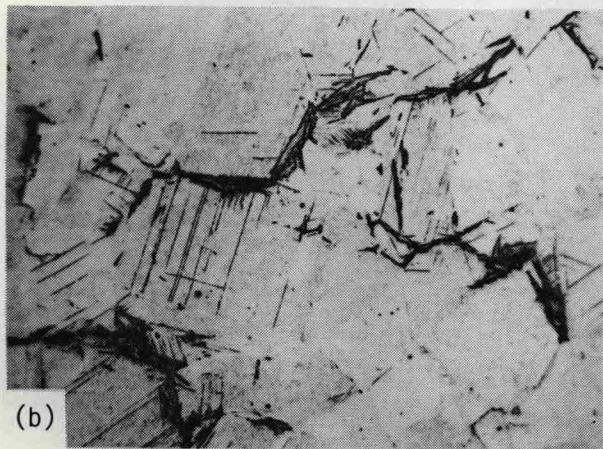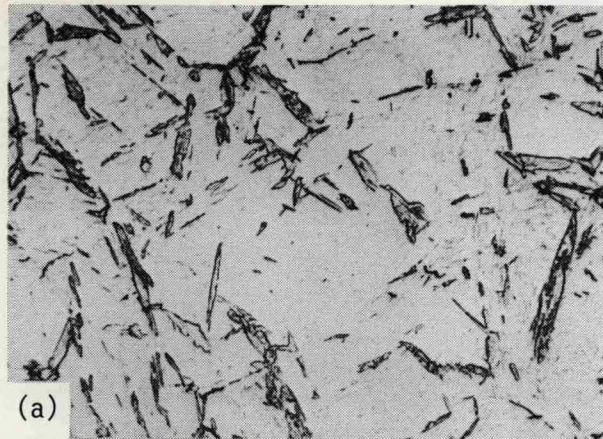
(a)

(b)

(c)   30μ

Photo. 6. Effect of pressure on microstructure of martensite in Fe-0.37%C-1.60%Cr alloy (C-3) quenched to various temperatures and then tempered under high pressure.
(a) quenched to 210°C at 29kbar,   (b) 160°C, 38.5kbar,
(c) 150°C, 41kbar,

Fig. 4. Effect of pressure on martensite structure in some alloys.

Photo. 7. Mixed structure of lenticular (L) and plate-like (E) martensite in Fe-0.35%C-1.51%Si alloy (S-3) quenched to 150 °C and tempered for at 300°C for 2min 41kbar.

site. However, no investigation was carried out on this change in the alloys used. If this change is similar to the difference in the volume between γ and α phases in iron caused with a decrease of temperature, it is assumed that this effect is stronger than that by alloying element, as the volume change increases with the depression of
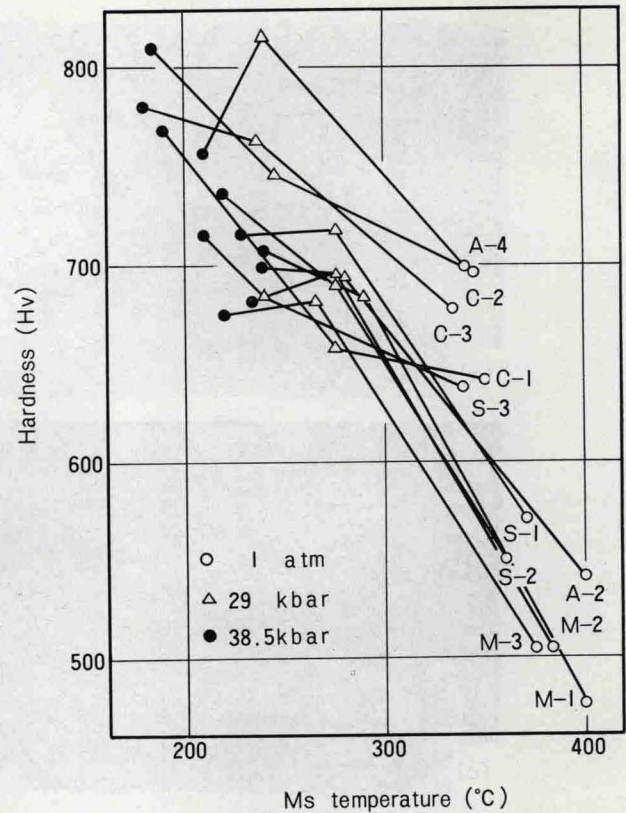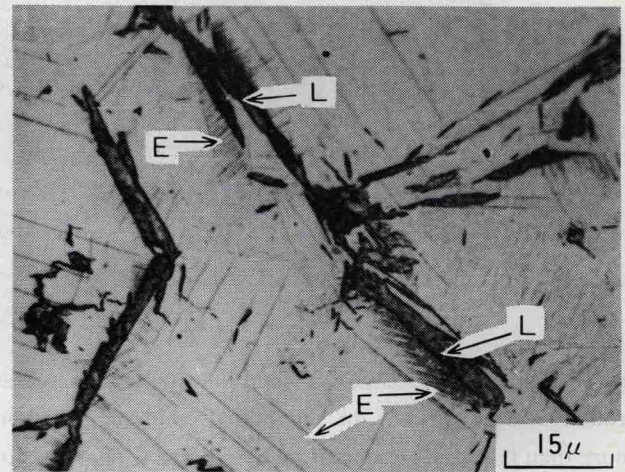
Ms-temperature. Consequently, it is thought that the effect of alloying element on the pressure dependency of Ms-temperature was not significantly observed.

4.2. Process of martensite transformation

The boundaries of γ, α and ε phases in the P-T diagram of pure iron are indicated in **Fig. 6** with the lines of T_0
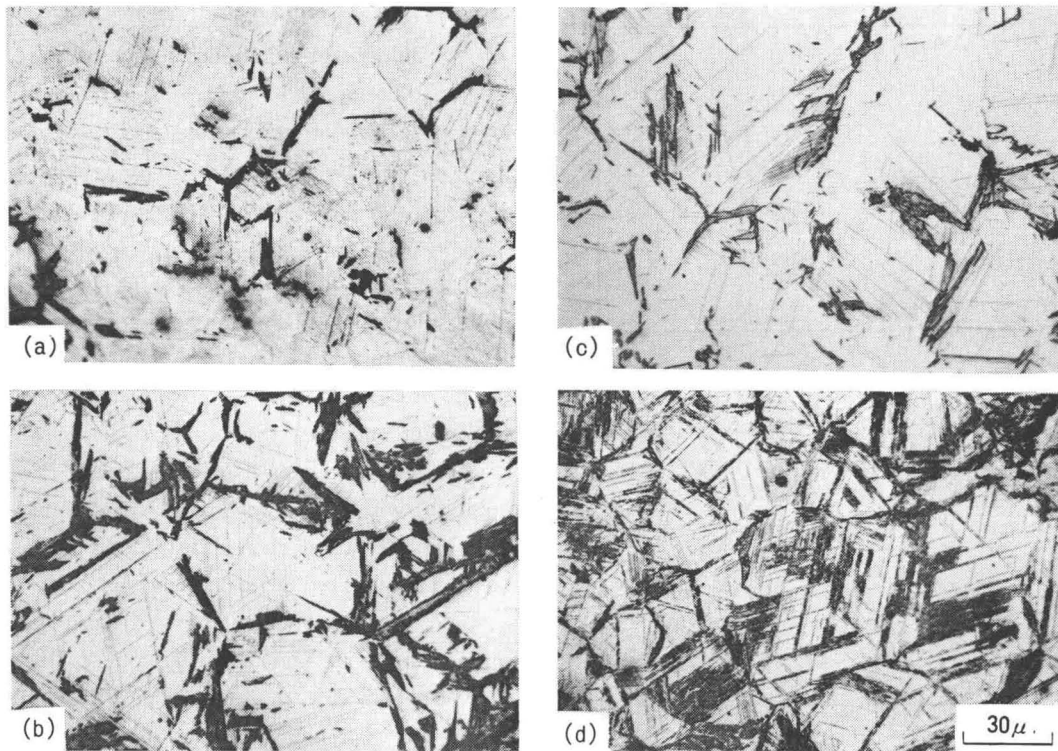
Photo. 8. Change of martensite structure in Fe-0.42%C (A-4) ((a) and (b)) and Fe-0.35%C-1.51%Si (S-3) ((c) and (d)) alloys at 38.5kbar, queeched to (a) 160°C, (b) 140°C, (c) 200°C and (d) 160°C.

$\gamma\rightleftarrows\alpha$, $T_o\gamma\rightleftarrows\varepsilon$ and $T_o\varepsilon\rightleftarrows\alpha$, which were determined on the basis of the thermodynamic analysis. It means that phases have the equal free energy on these lines. Therefore, T_o corresponds to the temperature where $\Delta G(T)=0$ at a given pressure, Thus, Ms-temperatures (Ms $\gamma\rightleftarrows\alpha'$, Ms $\gamma\rightleftarrows\varepsilon'$ and Ms $\varepsilon\rightleftarrows\alpha'$) at which martensitic phase of ε' or α' of iron is first formed by $\gamma\rightarrow\alpha'$, $\gamma\rightarrow\varepsilon'$, $\varepsilon'\rightarrow\alpha'$ transformations was determined from the relationship between the driving force and free energy change in each transformation as shown in the equation (2). In the present work, 300, 100 and 200 cal/mol were used as the driving forces in the corresponding transformations on the basis of the results reported already[5)~10)26)27)] The results of the calculations are shown as the various lines of Ms $\gamma\rightarrow\alpha'$, Ms $\gamma\rightarrow\varepsilon'$ and Ms $\varepsilon\rightarrow\alpha'$ in **Fig. 6.** Moreover, the relationship among these driving forces was assumed as follows.

$$\Delta G_v^{\gamma\rightarrow\alpha'}=\Delta G_v^{\gamma\rightarrow\varepsilon'}+\Delta G_v^{\varepsilon'\rightarrow\alpha'} \tag{3}$$

The equation (3) means that the triple point exists in martensitic transformation and the free energy of the phase is not affected by the process of the transformation.

The calculated Ms $\gamma\rightarrow\alpha'$ lines and Ms-temperatures measured at various pressures in Fe-0.2%C and Fe-0.42%C
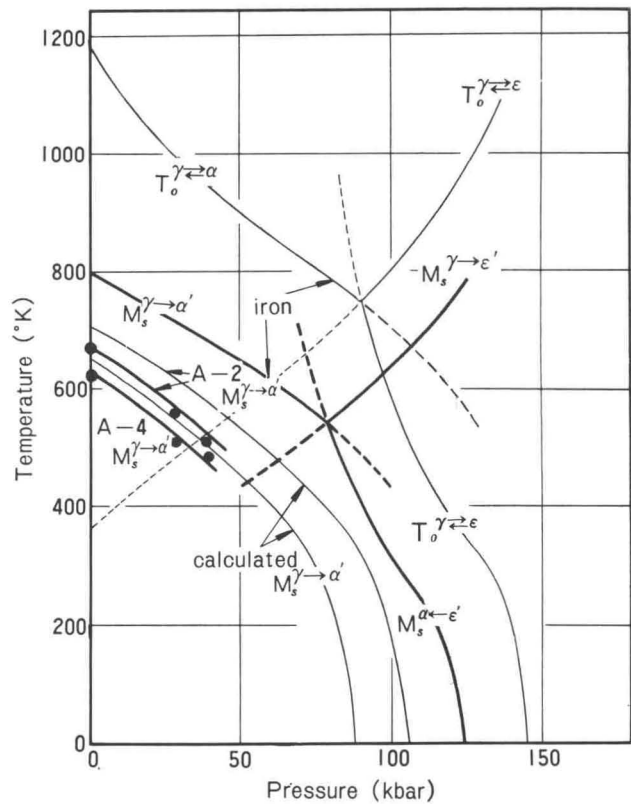

Fig. 5. Effect of Ms temperature on the microhardness of martensite formed in low alloys (Fe-0.3%C-X).
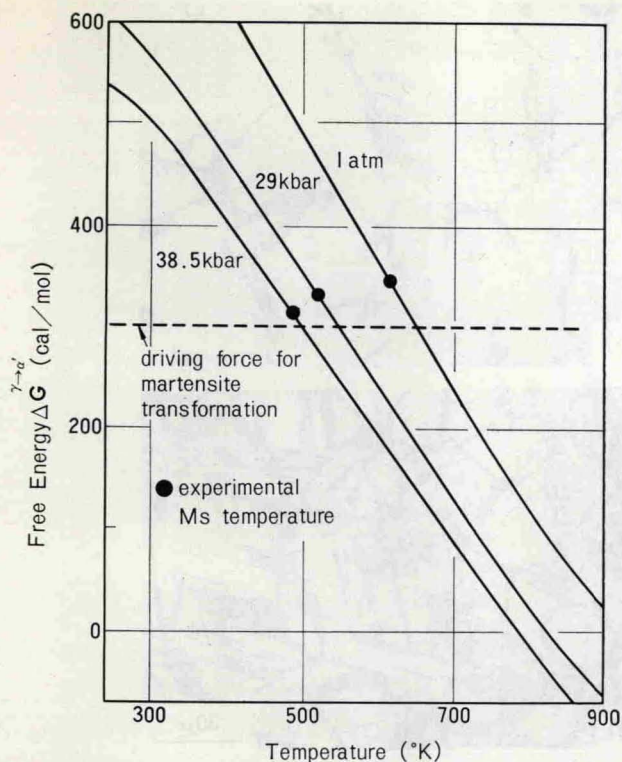
— 9 —

Fig. 6. P-T phase diagram of iron and effect of pressure on Ms-temperature of Fe-0.28%C (A-2) and Fe-0.42%C (A-4) alloys and iron.

alloys are indicated in **Fig. 6** in addition to the Ms lines of iron. A reasonable agreement between those is found in this figure. Moreover, Ms $^{\gamma \to \varepsilon'}$ lines on $\gamma \to \varepsilon'$ transformation of these alloys can be approximated by using those of iron. From the results mentioned above, 38.5 kbar is found to be the pressure close to the triple point at which
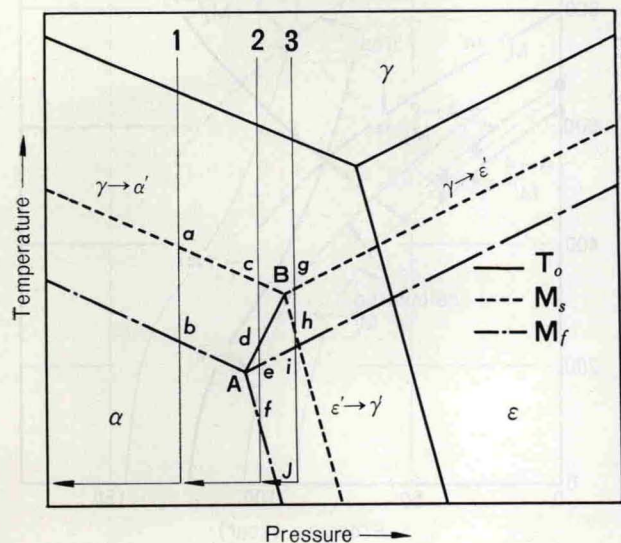

Fig. 7. A schematic illustration of P-T diagram on martensitic transformation in iron alloy.

three martensitic transformations occur simultaneously.

4.3. Change of martensite structure

It was attempted to explain the relation between the process of transformation and structure of martensite qualitatively, as shown in **Fig. 7** in which a P-T diagram with To, Ms and Mf of martensitic $\gamma \to \alpha'$, $\gamma \to \varepsilon'$ and $\varepsilon' - \alpha'$ transformations in an iron alloy is drawn schematically. If only the $\gamma \to \alpha'$ transformation at atmospheric pressure in the alloy occurs, the transformation takes a process of **1, 2** or **3** during cooling from γ phase under pressures. At the pressure of **1**, α' phase is primarily formed at Ms $^{\gamma \to \alpha'}$ point and then the volume fraction of α' phase increases with a decrease of temperature from Ms to Mf point (b) where the transformation is completed. In this case, the structural change from lath martensite to twin one was observed with an electron microscope and the change from packet structure to lenticular one was observed under an optical microscope. These phenomena may be as a result of pressurizing which might bring the depression of Ms-temperature and the same effect as that of the rapid cooling at atmospheric pressure. At the pressure of **2**, α' phase is primarily formed from γ phase at Ms $^{\gamma \to \alpha'}$ points (c) which is similar to that in the case of pressure **1**. Furthermore, when temperature decreases to point (d) across the AB line, which is connected between the two triple points of Ms and Mf, untransformed γ phase begins to transform to α' phase through ε' phase, and then at Mf $^{\gamma \to \varepsilon'}$ point (e) ε' and α' phases exist. Moreover, during cooling to Mf $^{\varepsilon \to \alpha'}$ point (f), ε' phase transforms to α' phase. Consequently, it seems that the martensite structure as shown in **Photo. 7** could be observed at 41 kbar which might correspond to the pressure of **2**. In this case, the plate-like structure due to the $\gamma \to \varepsilon'$ $\to \alpha'$ transformation was formed around the packet or lenticular structure which was primarily formed as a result of $\gamma \to \alpha'$ transformation. The easy formation of plate-like structure around the lenticular structure may be due to the instant increasing of pressure, caused by the $\gamma \to \alpha'$ transformation, at the boundary of α' phase. However, from the observation that only plate-like structure increased as the temperature decreased from Ms point as shown in **Photo. 8**, it is estimated that the pressure was not so high as 600 kg/mm² [28]. Under the pressure of **3**, during cooling from the γ phase, ε' phase forms primarily at Ms $^{\gamma \to \varepsilon'}$ point (g) and the ε' phase transforms to α' phase at Ms $^{\varepsilon' \to \alpha'}$ point (h). After further cooling, $\gamma \to \varepsilon'$ trans-

formation is completed at $Mf^{\gamma \to \varepsilon'}$ point (i) and during releasing of pressure, $\varepsilon' \to \alpha'$ transformation occurs because of passing through the $Mf^{\varepsilon \to \alpha'}$ point (j). In this work, both γ and ε' phases were not detected in the X-ray analysis of all the alloys pressurized. Consequently, the only α' phase existed in these alloys at atmospheric pressure as a result of $\gamma \to \varepsilon'$ and $\varepsilon \to \alpha'$ transformation during the release of pressure or during cooling under high pressure. It is thought that 41 kbar at which only plate-like structure was obtained corresponds to the condition of **3.**

On the other hand, the $\gamma \to \varepsilon' - \alpha'$ transformation is observed in Fe-Mn and Fe-Ni-Cr alloys even at atmospheric pressure.[23)4)] From this results, it can be considered that this pressure for these alloys is equivalent to condition of **3** in **Fig. 7.** This fact means that the observation of the transformation caused in high alloy at atmospheric pressure is also possible in low alloy under high pressure.

It was described above that the plate-like structure of martensite is formed after $\gamma \to \varepsilon' \to \alpha'$ transformation under high pressure. Here, the following two processes producing this structure will be discussed. The first is a case in which the plate-like structure will be formed during tempering of ε' phase at 300°C, which was precipitated in $\gamma \to \varepsilon'$ transformation during prior quenching. However, when the ε' phase is reheated at 300°C, it must be transformed to γ phase at this temperature. Thus, the first case is not likely to occur. In the second case, considered that the structure will be as a result of formation of twin during the relief of strain which is accumulated around the lenticular structure due to the volume expansion in $\gamma \to \alpha'$ transformation. However, this process is also un-

likely to occur, because as the twin forms without the volume change, the pressure does not enhance the formation of twins.

Finally, the results were summerized schmaticaly on P-T diagram for low carbon alloy in **Fig. 8.** From this figure, the relationship between the process of transformation and various martensite structure, could be understood.

5. Conclusion

(1) The Ms-temperature was lowered approximately 40 °C/10 kbar in all alloys pressurized in this experiment and its tendency was not singniticantly affected by alloying elements.

(2) The difference between measured Ms-temperature and calculated one under the conditions of various was fluctuated between 30 to 60°C. It is, however, possible to estimate Ms-temperature of low alloys by using Predmore's equation.

(3) The microhardness of martensite structures increases with an increase of pressure. This might be as a result of the lowering of Ms-temperature by prsssure, accompanying with the change of martensite structure.

(4) The structural changes of martensite, caused by pressurizing can be explained qualitatively by P-T diagram of iron. With an increase of pressure the change from packet structure to plate-like one was observed in the alloys containing carbon less than 0.3%. In the alloys containing carbon more than 0.3%, the change from mixed lenticular and plate-like structure to plate-lke structure was observed. It is thought that the plate-like structure was observed in the martensite formed by $\gamma - \varepsilon' - \alpha'$ transformation. The pressure at which this structure appears, is affected by alloying elements and the effect becomes stronger in the order of Mn, Cr and Si addition.

Fig. 8. A schematic illustration of the region with various types of martensite on P-T diagram for a low carbon alloy.

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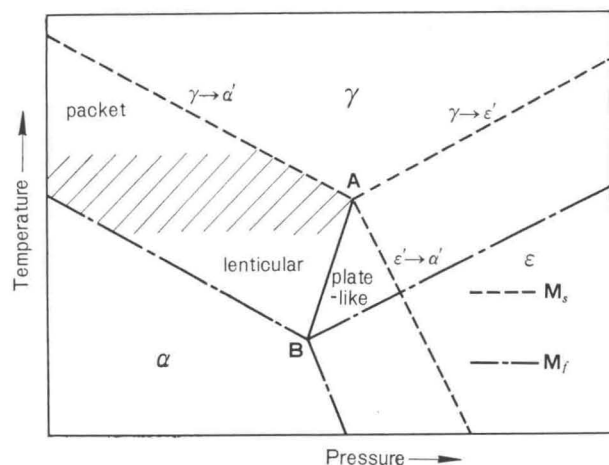8) J. S. Pascover and S. V. Radcliffe: Acta Met., **17** (1969) 3, 321.

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Appendix

Predmore's equation used in this study is as follows:

$$\Delta G^{\alpha \to \gamma'}_{(x, T, P)} = 1 - (X_{Cr} + X_C + X_{Si} + X_{Mn})$$
$$(1\,202 - 2.63 \times 10^{-3} T^2 + 1.54 \times 10^{-6} T^3)$$
$$+ X_{Cr} (460 + 1.0 T) + X_{Cr} (1 - X_{Cr})(-2\,800 + 0.75 T)$$
$$+ 450 X_{Si}$$
$$- 2\,700 X_{Mn}$$
$$+ RT \left[X_C \ln\left(\frac{3 - X_C (3+z)}{1 - 6 X_C}\right) + \left(\frac{1 - X_C}{3}\right) \ln\left(\frac{1 - 6 X_C}{1 - X_C}\right) \right.$$
$$\left. - \frac{3(1 - X_C)}{z} \ln\left(\frac{3 - X_C (3+z)}{3(1 - X_C)}\right) \right]$$
$$- 24. P [\Delta V^{\alpha' \to \gamma}_{293K} - 2 \times 10^{-4} (T - 293)] \cdots\cdots\cdots\cdots(1)$$

List of Symbols

$\Delta G^{\alpha' \to \gamma}_{(x, T, P)}$	Free energy change for $\alpha \to \gamma$
T	Temperature (°K)
P	Pressure (kbar)
X_{Cr}	Atomic fraction of solute (Cr)
X_C	Atomic fraction of solute (C)
X_{Si}	Atomic fraction of solute (Si)
X_{Mn}	Atomic fraction of solute (Mn)
R	Gas constant
z	Exclusion parameter ($z = s - 1$)
s	Number of neighboring sites excluded by the occupancy of a given interstitial site
$\Delta V^{\alpha' \to \gamma}_{293K}$	Change in molar volume for $\alpha \to \gamma$ [6]