

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

Mitsutane FUJITA, Iku UCHIYAMA, and Masatoshi SUZUKI

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.

(Received May 14, 1974)

1. Introduction

It is well known that the $\alpha \rightarrow \epsilon'$ transformation was induced by pressurizing to more than 130kbar in pure iron¹⁾²⁾ and also ϵ phase was observed in some alloys such as Fe-Mn³⁾ and Fe-Ni-Cr⁴⁾ 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-Mn⁹⁾ alloys and the low alloy steels¹⁰⁾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 $\gamma \rightleftharpoons \alpha + \text{Fe}_3\text{C}$ 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 kbar. 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.

* Original: Tetsu-to-Hagane, 60 (1974) 1, 58, (in Japanese).

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 levels up to 1.5%. These materials are similar to those used for the investigation¹³⁾ 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 alloys¹⁰⁾¹⁵⁾ containing Mn of more than 10% and in the Fe-4.2%C-1.5%Si alloy¹⁶⁾ 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 $\gamma \rightarrow \epsilon' \rightarrow \alpha'$ transformation.⁸⁾ Consequently, the addition Mn, Si and Cr is expected to lower the transition pressure for $\alpha \rightarrow \epsilon'$ 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. Kenneford¹⁴⁾ examined the effect of some elements on the volume change for $\gamma \rightleftharpoons \alpha + \text{Fe}_3\text{C}$ transformation at A_{c3} 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 $\gamma \rightleftharpoons \alpha + \text{Fe}_3\text{C}$ 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 $\gamma \rightleftharpoons \alpha + \text{Fe}_3\text{C}$ 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 maximum 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 Radcliffe et al.⁶⁾ At first, two specimens with 3mm in diameter and 3mm 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 reported¹⁸⁾ that the structure obtained by this method was changed by tempering temperature and holding time and it became difficult to distinguish 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⁾¹⁸⁾

3. Results

3.1. Ms-temperature

Some results on Ms-temperatures measured at 1 atm,