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The Effect of Niobium on the Heat Treatment of Fe-C-Cr Alloys

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Fe-C-Cr 합금의 열처리에 대한 Niobium 첨가의 영향

백 홍 구

개 요

Fe-C-Cr 합금의 열처리에 대한 Nb첨가의 영향이 nondestabilization 열처리조건과 destabilization 열처리조건하에서 연구되었다. Nb의 첨가는 주방상태에서의 Pearlite 또는 austenite 기지조직의 경도를 증가시키며, nondestabilization 열처리조건에서는 조직이 austenite와 secondary carbide로 구성되며, 주방상태에 비하여 경도는 secondary carbide의 정출로 인하여 증가되었다. Destabilization 열처리조건하에서는 조직이 martensite와 secondary carbide로 구성되며 austenite의 martensite로의 변태와 secondary carbide에 의한 기지조직의 강화로 인하여 경도가 현저히 증가되었다. 한편, Nb의 첨가는 austenite의 martensite의 변태와 secondary carbide의 형성 및 생성량에는 영향을 미치지 않았다.

1. Introduction

High chromium irons are widely used in industry as a wear resistant materials and corrosion resistant materials. It is known[1,2,3,4,5] that additional alloyings of high chromium irons with carbide forming elements(V, W, Nb, Ti) signifcantly affect the mechanical properties, chemical compositions and dispersion of carbides as well as the strength of the matrix. These cause a change in the wear resistant and toughness of high chromium irons.

For wear resistant service, high chromium irons are generally utilized in the martensitic condition and the optimum choice for a matrix is a hard, high carbon martensite, possibly dispersion hardened by secondary carbides. In most circumstances, in order to obtain a fully martensitic transformation, it is necessary to destabilize the structure by heat treatment the cast-ing within the temperature range 920 to 1000°C (a process termed destabilization). This decrease both the chromium and the carbon contents of the matrix due to secondary carbide precipitation and increases hardenability of high chromium iron. The precipitation of secondary carbides changes the composition of the austenite, alters its transformation characteristics, retards the pearlitic transformation, make possible a banite transformation and permits a martensitic transformation in all alloys.

Some investigators[7,8,9,10] provided much of the available data on the effect of alloy elements during heat treatment of high chromium irons. However, there has been very little fundamental research conducted on the effect of niobium on the solidification structure during heat treatment of high chromium irons. Guesser[11] reported that niobium additions to 1% allow decreasing molybdenum content without speeding up to the pearlite transformation at 700°C In the present work,

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the effect of niobium on the heat treatment of Fe-15%Cr alloy with 2.4 to 3.4% C and 0 to 2.15% Nb were studied.

2. Experimental Procedures

Heats produced in this study were produced in a 23kg silica lined high frequency induction furnace. The initial charge consisted of clean pig iron and steel scrap in the requisite proportions to adjust the chemical composition. After ensuring that the initial charge consisting of pig iron and steel scrap was in a molten condition, slag removed, and then ferro-chromium and other alloying elements were added.

Table 1. Chemical composition of specimens

Specimen NO	Chemical Composition						
	%C	%Mn	%Si	%Cr	%Nb	%Mo	%Ti
1-1	3.44	0.112	0.42	16.09	0.00	0.003	0.031
1-2	3.34	0.119	0.43	15.90	0.65	0.006	0.032
1-3	3.27	0.128	0.43	15.79	1.32	0.010	0.039
1-4	3.23	0.134	0.46	15.72	1.95	0.012	0.048
1-5	3.14	0.138	0.47	15.44	2.00	1.250	0.047
1-6	3.05	0.143	0.48	15.10	1.95	2.380	0.045
1-7	3.01	0.149	0.49	14.85	2.00	3.310	0.044
2-1	2.82	0.165	0.41	16.54	0.00	0.013	0.019
2-2	2.81	0.170	0.42	16.41	0.63	0.017	0.027
2-3	2.72	0.181	0.44	16.13	1.33	0.020	0.035
2-4	.2.70	0.190	0.44	15.59	1.83	0.023	0.040
2-5	2.58	0.191	0.44	15.19	1.95	2.340	0.040
2-6	2.50	0.202	0.44	14.76	1.82	3.160	0.037
3-1	2.44	0.336	0.29	15.89	0.00	0.033	0.019
3-2	2.51	0.320	0.29	15.19	0.63	0.033	0.025
3-3	2.42	0.311	0.30	15.36	1.45	0.043	0.034
3-4	2.38	0.307	0.32	15.28	2.13	0.053	0.041
3-5	2.31	0.295	0.32	15.01	2.05	1.370	0.038
3-6	2.31	0.277	0.30	14.85	2.10	2.520	0.036
3-7	2.29	0.275	0.32	14.65	2.15	3.580	0.035
4-1	3.07	0.246	0.28	14.97	0.11	0.088	0.021
4-2	2.95	0.267	0.33	14.85	0.90	0.092	0.034
4-3	2.89	0.292	0.36	14.30	0.88	0.089	0.242
4-4	2.85	0.300	0.40	14.30	1.70	0.093	0.164
4-5	2.80	0.306	0.43	14.22	2.00	0.096	0.145

The melts were superheated in the furnace up to 1593°C and were poured into the eutectometer sample MK V. By employing a split heat technique, 25 iron alloys were produced. A summary of the chemical compositions of the heats is presented in Table 1. The average final chemistry of these heats was 15% Cr(14.22 to 16.54%) which included variations in actual analysis.

Specimens for heat treatment were taken from the eutectometer samples MK V in the as cast condition and cut into half round of 6mm thickness. Specimens which were austenitic or pearlitic in the as cast condition were heated to 1125°C for 20 minutes and subsequently air cooled(a process termed nondestabilization). Specimens which were austenitic in the as cast condition were heated to 975°C for 20minutes and subsequently air cooled(a process termed destabilization).

The morphology of carbides was examined using conventional optical microscope and were then deep etched examined using the scanning electron microscope(SEM). The matrix was dissolved with a solution of 73% HCL, 25% HNO₃ and 2% HF.

To measure the microhardness a series of 10 were taken for each sample.

3. Experimental Results and Discussions

3-1. Effect of Niobium on the As-Cast Condition

To investigate the effect of the niobium content on the matrix structure, the microhardness values were measured from the samples. Table 2 showed the hardness values of the matrix structures. It was observed from Table 2 that the addition of molybdenum slightly increased the hardness of austenite matrix(compare specimen no ; 1-5 to 1-7, 2-5 to 2-7, 3-5 to 3-7). It might be explained by the partition of molybdenum to austenite. We found from the previous experiment[12] that the partition of molybdenum to austenite slightly increased with an increase in

Table 2. Hardness of as-cast matrix

Sample number	Microhardness(HV 50G)
1-1	578
1-2	571
1-3	644
1-4	669
1-5	386
1-6	429
1-7	426
2-1	370
2-2	374
2-3	387
2-4	399
2-5	409
2-6	426
3-1	363
3-2	377
3-3	387
3-4	401
3-5	408
3-6	424
3-7	427

the molybdenum content of the alloy. The increased partition of the molybdenum content induced the solid solution hardening of austenitic structure. Therefore, the increased solid solution hardening slightly increased the hardness of austenitic structure.

On the other hand, it was determined from the analysis of Table 2 that the hardness values of pearlitic structure(specimen no ; 1-1 to 1-4) and austenitic structure(specimen no ; 1-5 to 3-7) slightly increased with an increase in the niobium content of the alloy. We compared the interlamellar spacings of pearlite by using SEM but we could not find the significant variations of the interlamellar spacing with an increase in the niobium content of the alloys. It was observed from the previous experiment[12] that the partition coefficient of niobium to austenite was in the range of 0-0.02 and very small value of the partition coefficient indicates that austenite contained little niobium. Therefore, the addition of niobium did not appear to affect the transformation of the matrix structure because of no partition of niobium to austenite. It is not clear, at present, how the hardness values of pearlitic or austenitic structures increased with the addition of niobium. One possibility could be that the amount of niobium carbide increased with an increase in the niobium content of the alloy. The increased amount of niobium carbide might increase the hardness of the matrix structure.

3-2. Effect of Niobium on Nondestabilization

The samples(specimen no ; 1-1 to 1-7) were heat treated by austenizing at 1125°C for 20minutes and air cooling. The heat treatment was designed to reaustenize the pearlitic structure. After nondestabilization the microstructures consisted of austenite and secondary carbides as seen in the optical and the scanning electron micrographs of Figures 1 and 2. It was determined from the microstructures of Figures 1 and 2 that the temperature(1125°C) and the holding time(20minutes) adopted for reaustenizing the pearlitic structure were enough to reaustenize the pearlitic structure and to obtain austenitic structure by air cooling.

It was determined from these experiments that the amount of secondary carbides depended on the as-cast structure. The samples which were pearlitic structure in the as-cast condition(specimen no ; 1-1 to 1-4) consisted of larger amounts of secondary carbides than samples which were austenitic structure in the as-cast condition (specimen no ; 1-5 to 1-7). It can be explained that when the pearlitic structure was held for 1125°C and 20minutes, the first transformation was that of ferrite to austenite. After this transformation, the M_3C carbide transformed to M_7C_3 carbide because M_7C_3 carbide is more stable phase[13]. It was confirmed by Maratray[13]. The samples which consisted of the pearlitic structure underwent transformation to austenite and secondary carbides and it induced larger amounts of secondary carbides. After non-
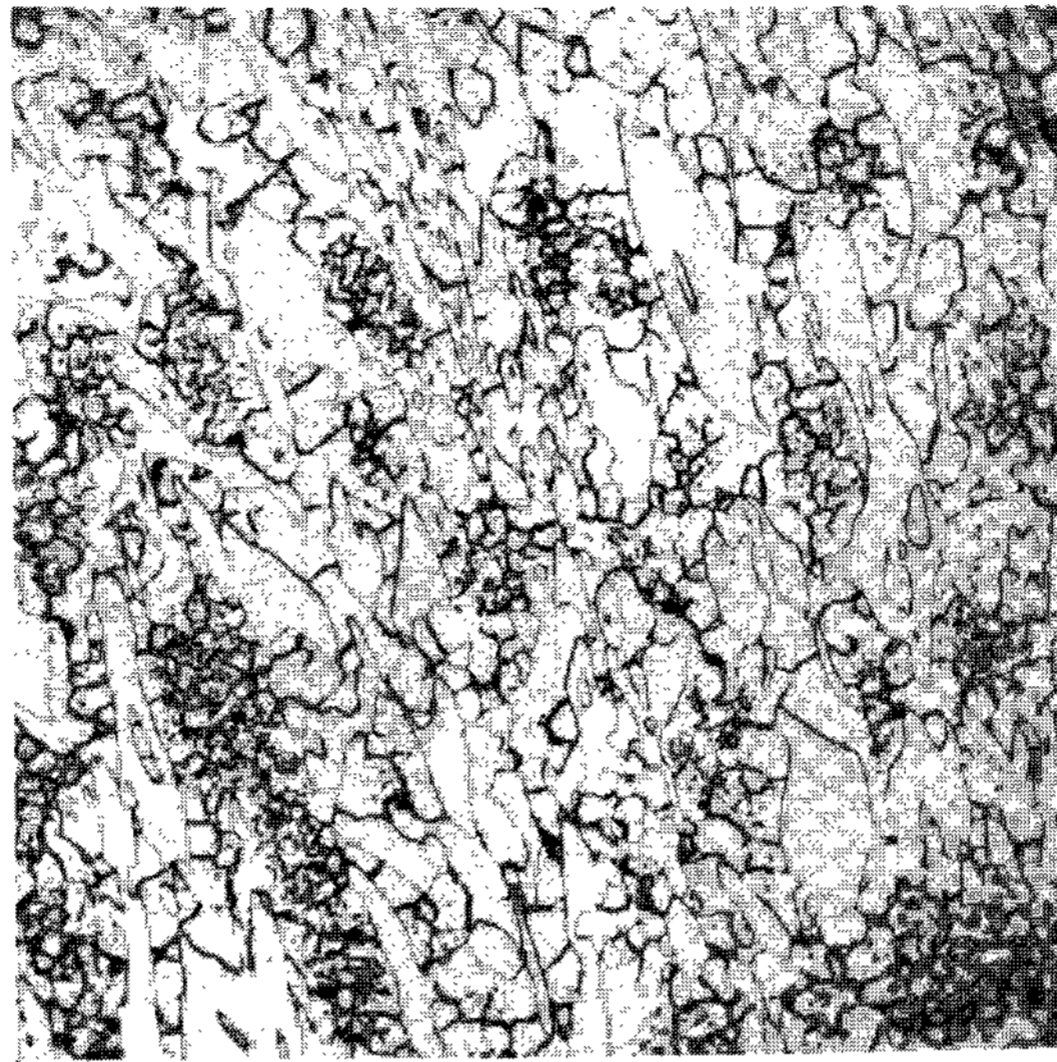
(a)
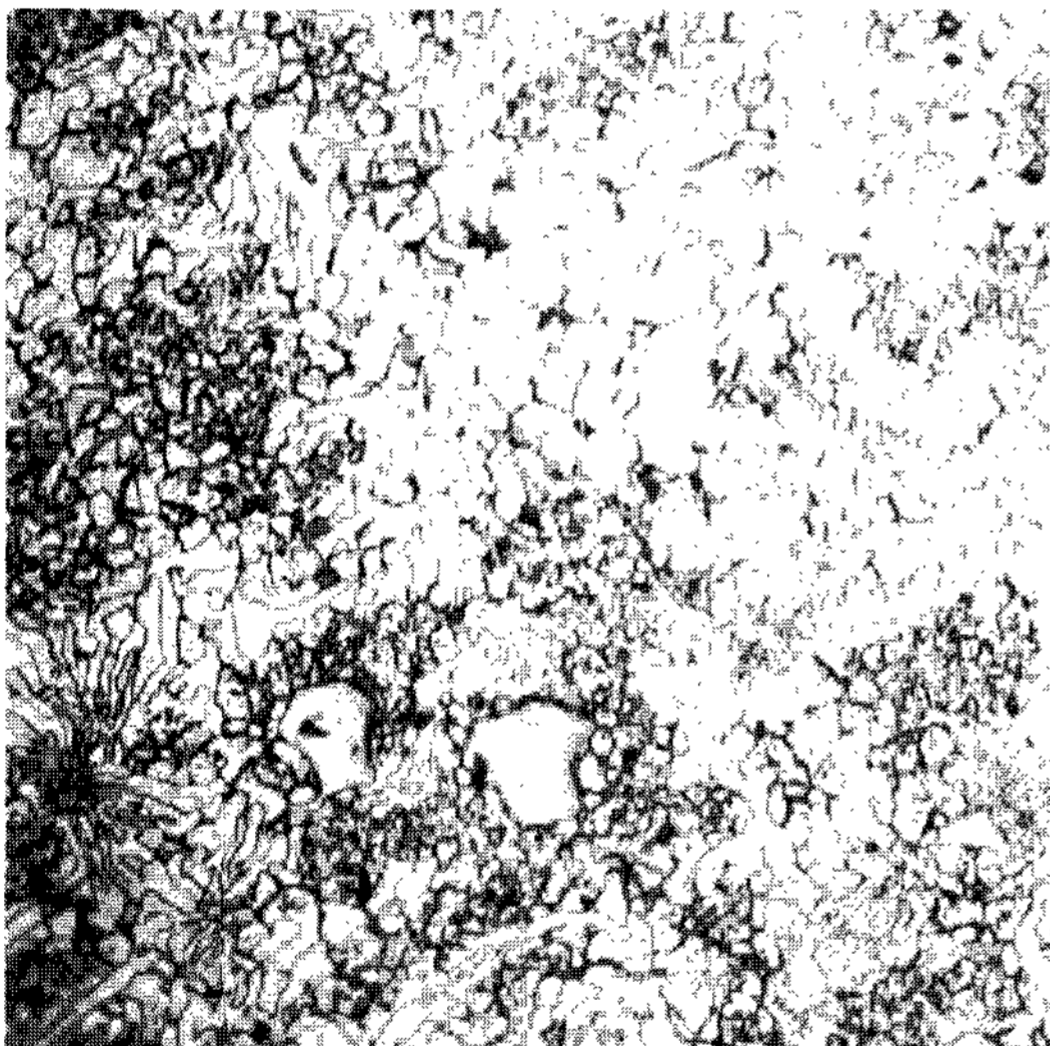
(b)
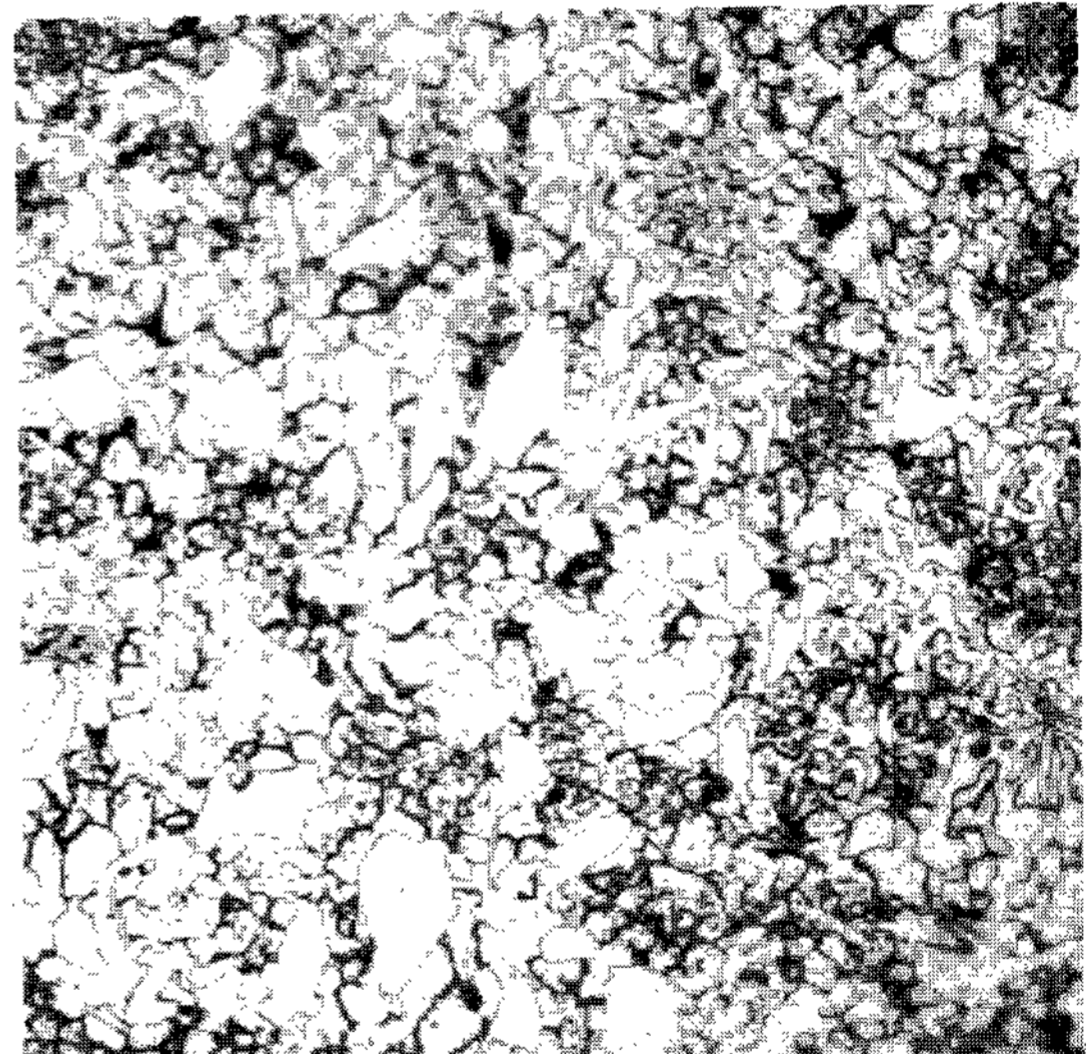
(c)

Fig. 1. Microstructures After Nondestabilization.
(a) No ; 1-1   (b) No ; 1-4   (c) No ; 1-7
Etched in 4% Nital. Magnification, 500X.

destabilization the secondary carbides so formed were spheroids finely distributed through the matrix as seen in Figures 2.

Table 3 showed the hardness values of the matrix structure after nondestabilization. It was observed from Table 3 that after nondestabilization, the samples which were pearlitic structure in the as cast condition showed higher hardness than the samples which were austenitic structure in the as cast condition. The samples which were pearlitic structure were transformed to austenite and secondary carbides during nondestabilization but the samples which were austenitic structure were free of transfor-
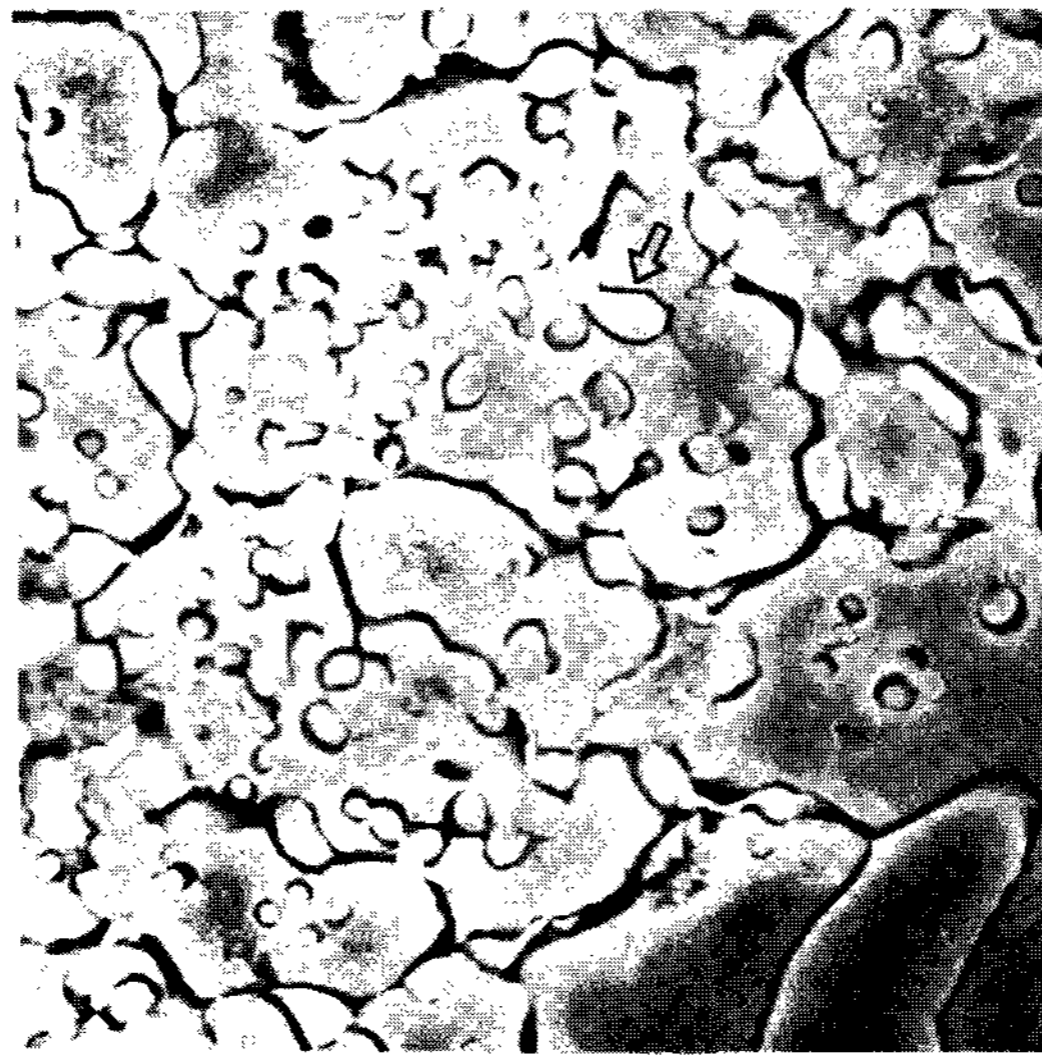
(a)
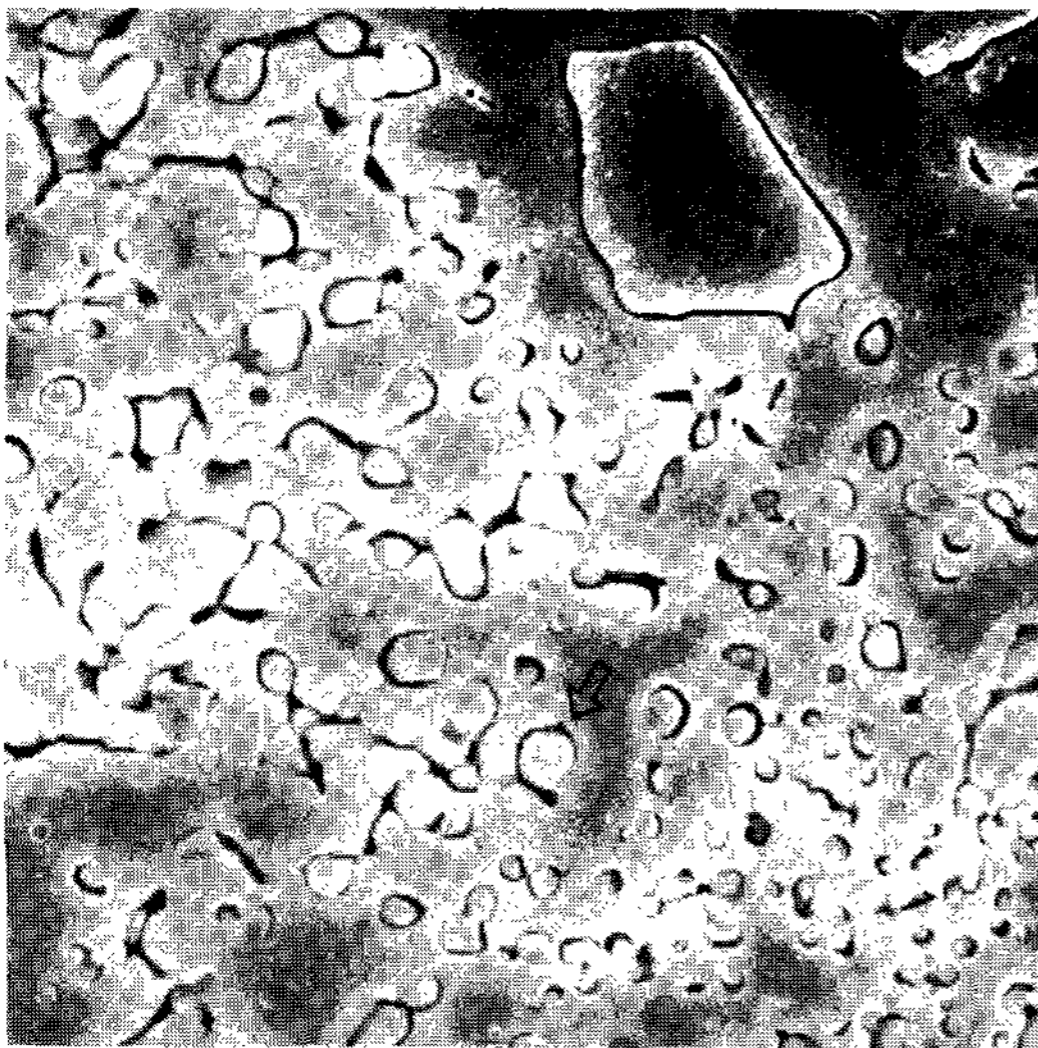
(b)

(c)

Fig. 2. Scanning Electron Micrographs After Nondestabilization
(a) No ; 1-1   (b) No : 1-4   (c) No ; 1-7.   Deep Etched.

mation and they did not have larger amounts of secondary carbides(compare Figure 3a, b and c). So it was determined from the results of Table 3 and Figure 2 that higher hardness of samples(specimen no ; 1-1 to 1-4) came from a larger amount of secondary carbides.

On the other hand it was observed from Table 3 that the addition of niobium slightly increased the hardness of matrix (compare specimen no ; 1-1 to 1-4). It may be explained that the amount of niobium carbide increased with an increase in the niobium content of the alloy. The increased amount of niobium carbide might increase the hardness of matrix. But it was determined from these experiments that the addition of niobium did not appear to affect

Table 3. Hardness of the matrix of nondestabilized condition

| Sample number	Microhardness(HV 50G)
1-1	711
1-2	721
1-3	783
1-4	792
1-5	679
1-6	677
1-7	682

the transformation to austenite and secondary carbides during nondestabilization of the present work. The amount of secondary carbides did not appear to change with an increase in the niobium content of the alloys as seen in Figure 2a and b.

3-3. Effect of Niobium on Destabilization

The samples(specimen no ; 2-1 to 3-7) were heat treated at 975°C for 20minutes and air cooling. The heat treatment was desgined to precipitate the secondary carbides and the austenite could transform to martensite on cooling, *providing the samples have enough hardenability* to avoid forming pearlite. It was observed from Figures 3 and 4 that after destabilization(975°C, held 20minutes and air cooling), the matrix structures consisted of martensite and secondary carbides. The secondary carbides were shown by arrows in Figure 4. Two basic requirements must be met for the transformation of austenite to martensite to occur in Fe-C-Cr alloys and Fe-C-Cr-Nb alloys of the present work. First, the concentration of alloying elements in the matrix, particularly carbon content, must be lowered from the high levels present following solidification, and, second, there must be adequate hardenability to avoid the transformation of austenite to ferrite-carbide constituents such as pearlite or bainite. In the present work the first requirement involved the precipitation of secondary carbide as seen in Figure 4. The austenite formed on solidification was saturated with
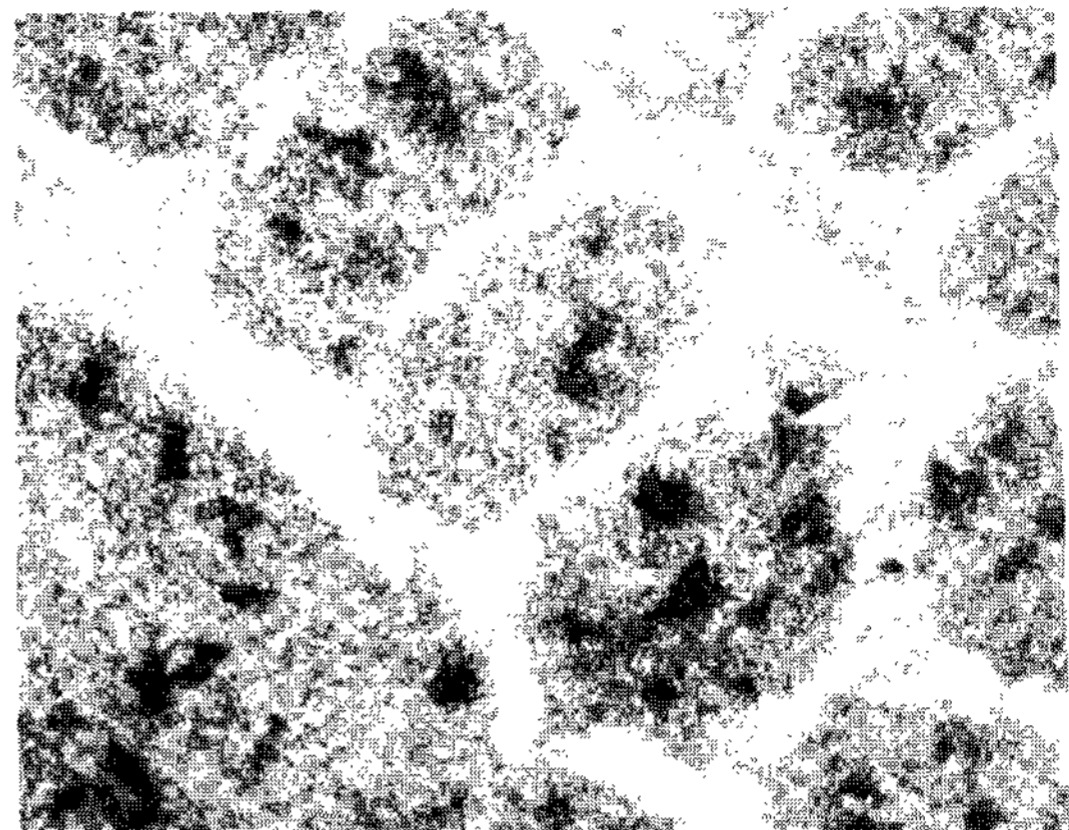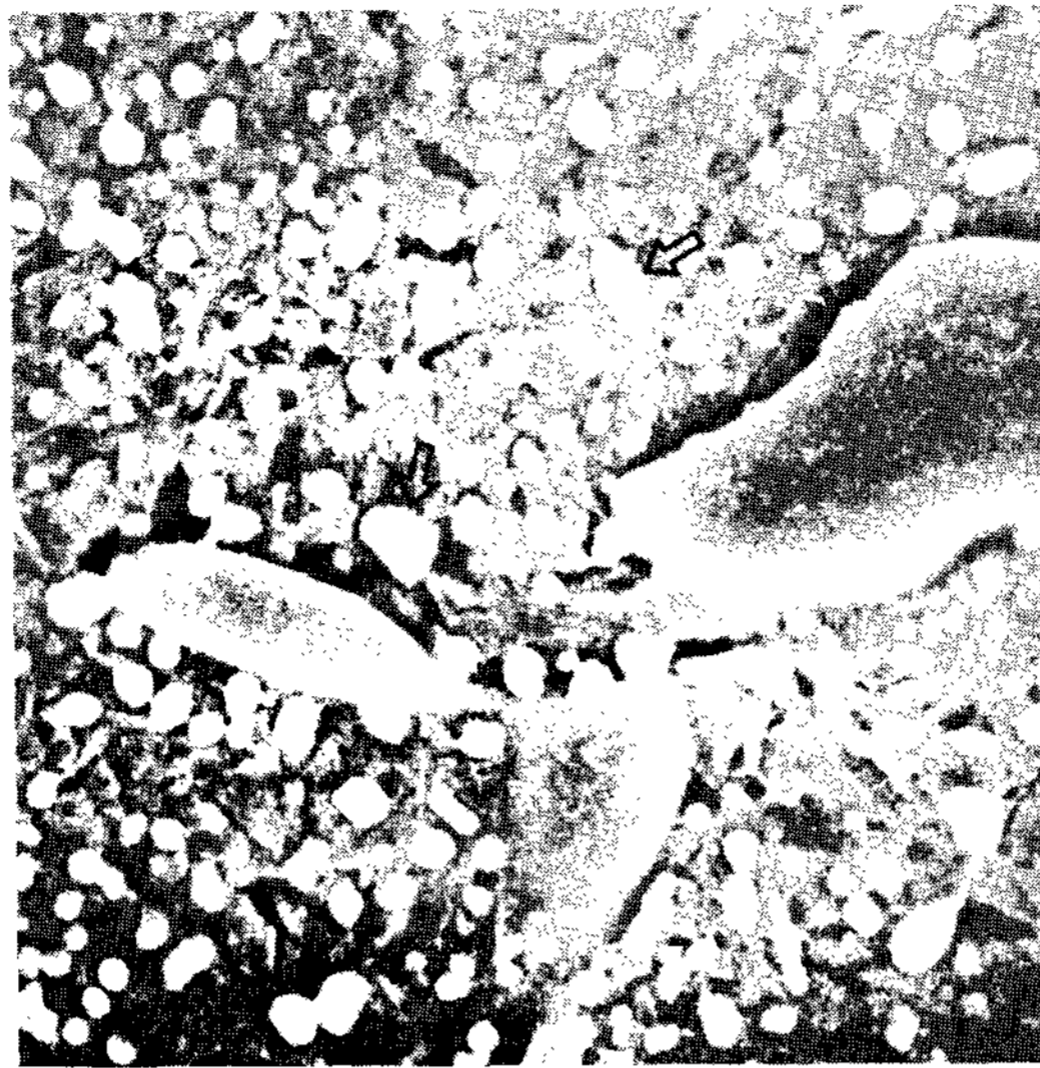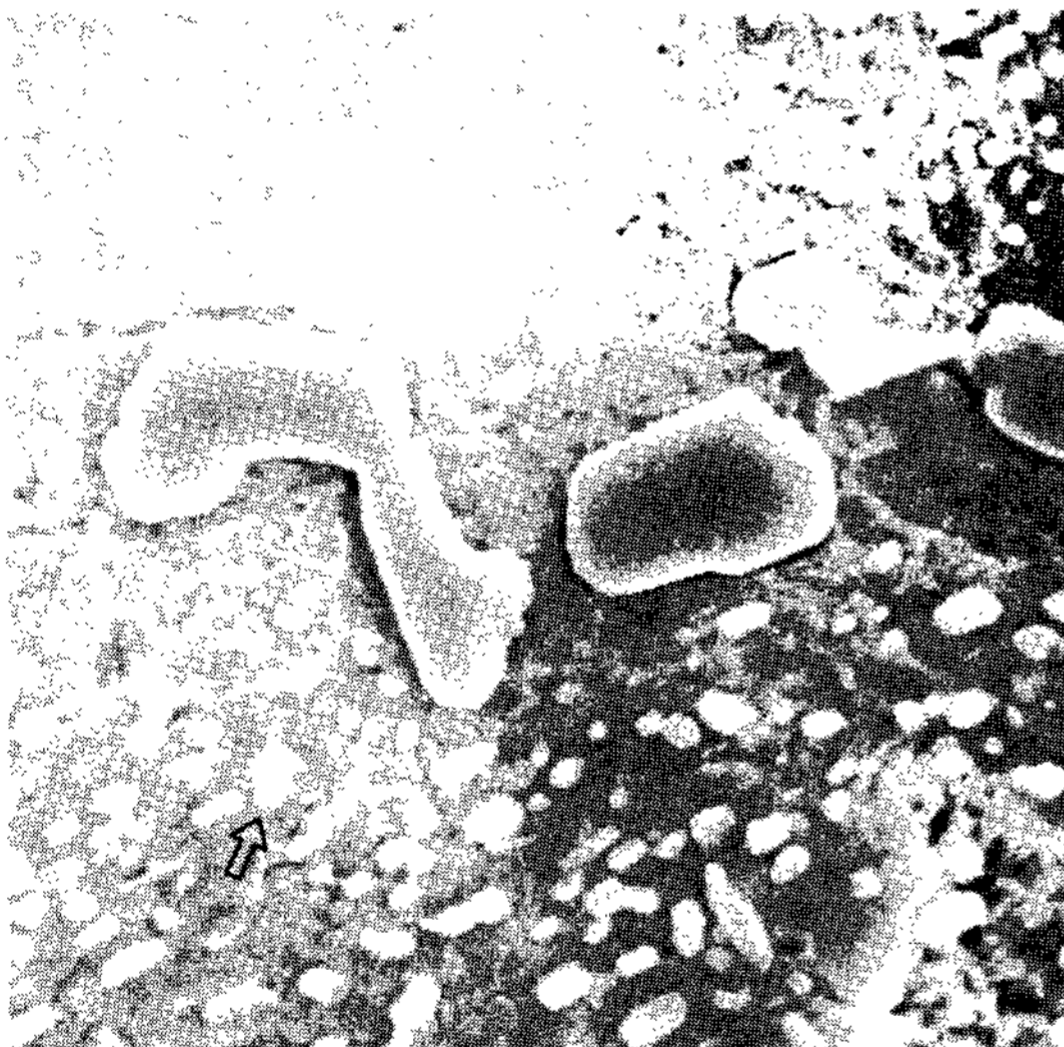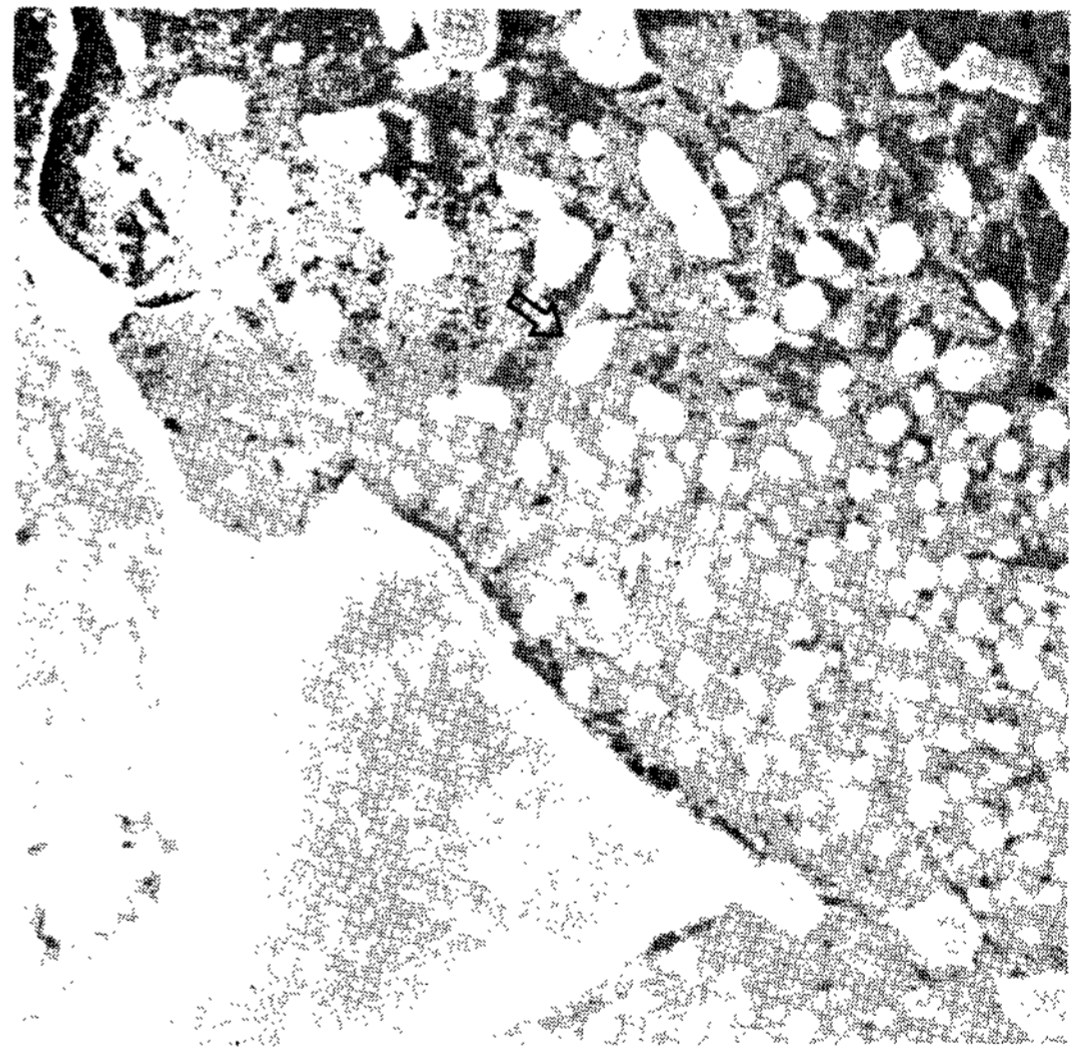

(a)
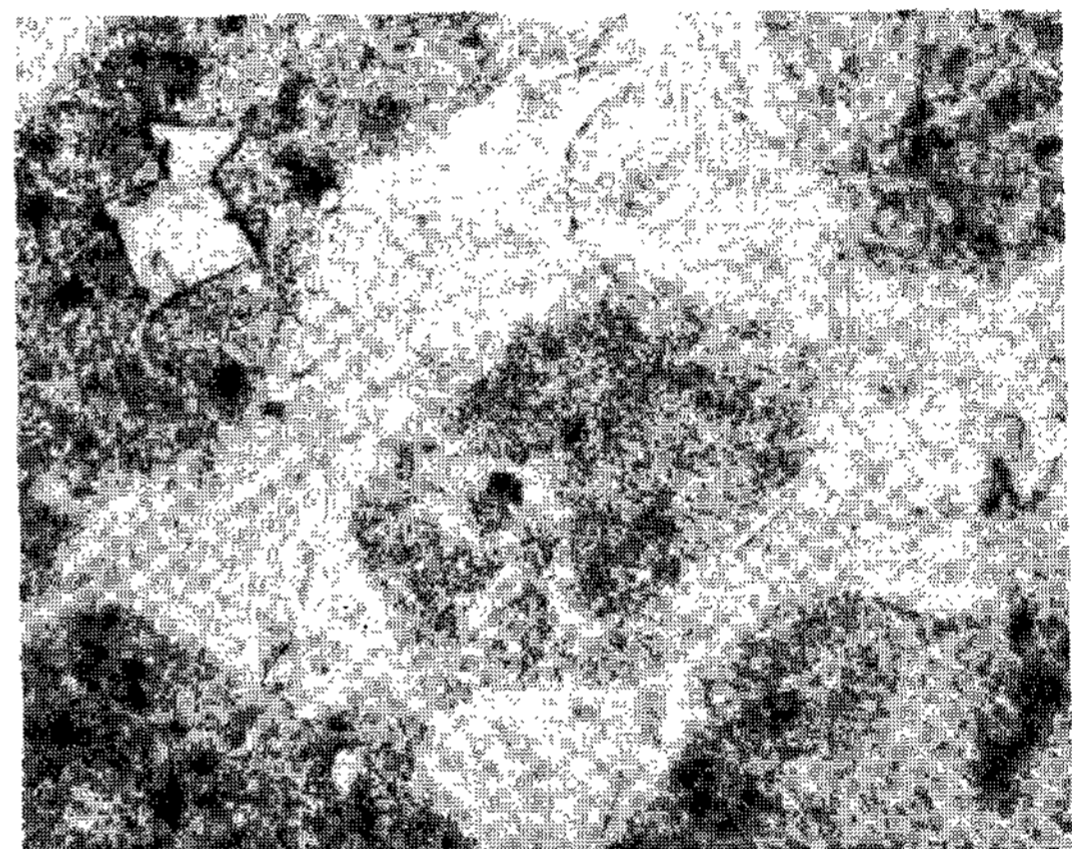
(b)

(c)

Fig. 3. Microstructures After Destabilization.
(a) No ; 3-1　(b) No ; 3-4　(c) No ; 3-7
Etched in 4% Nital. Magnification, 500X.

(a)

(b)

(c)

Fig. 4. Scanning Electron Micrographs After Destabilization.
(a) No ; 3-1   (b) No ; 3-4   (c) No ; 3-7. Deep Etched.

carbon, chromium and other alloying elements and was very stable in the previous experiment[12]. After heating to high temperature(975℃, held 20momutes), the chromium and carbon were precipitated as secondary carbides, reducing alloy content and therefore the stability of austenite. So after heating and precipitating secondary carbides in the matrix, both the chromium and carbon contents of the matrix were decreased due to the precipitation of secondary carbides. It made an austenite transformation to martensite on cooling as seen in Figures 3 and 4. It is in agreement with the results of Maratray[7] and Cias[10] even if their systems are Fe-C-Cr alloys. Maratray[7] determined continuous cooling transformation(CCT) diagrams. Figure
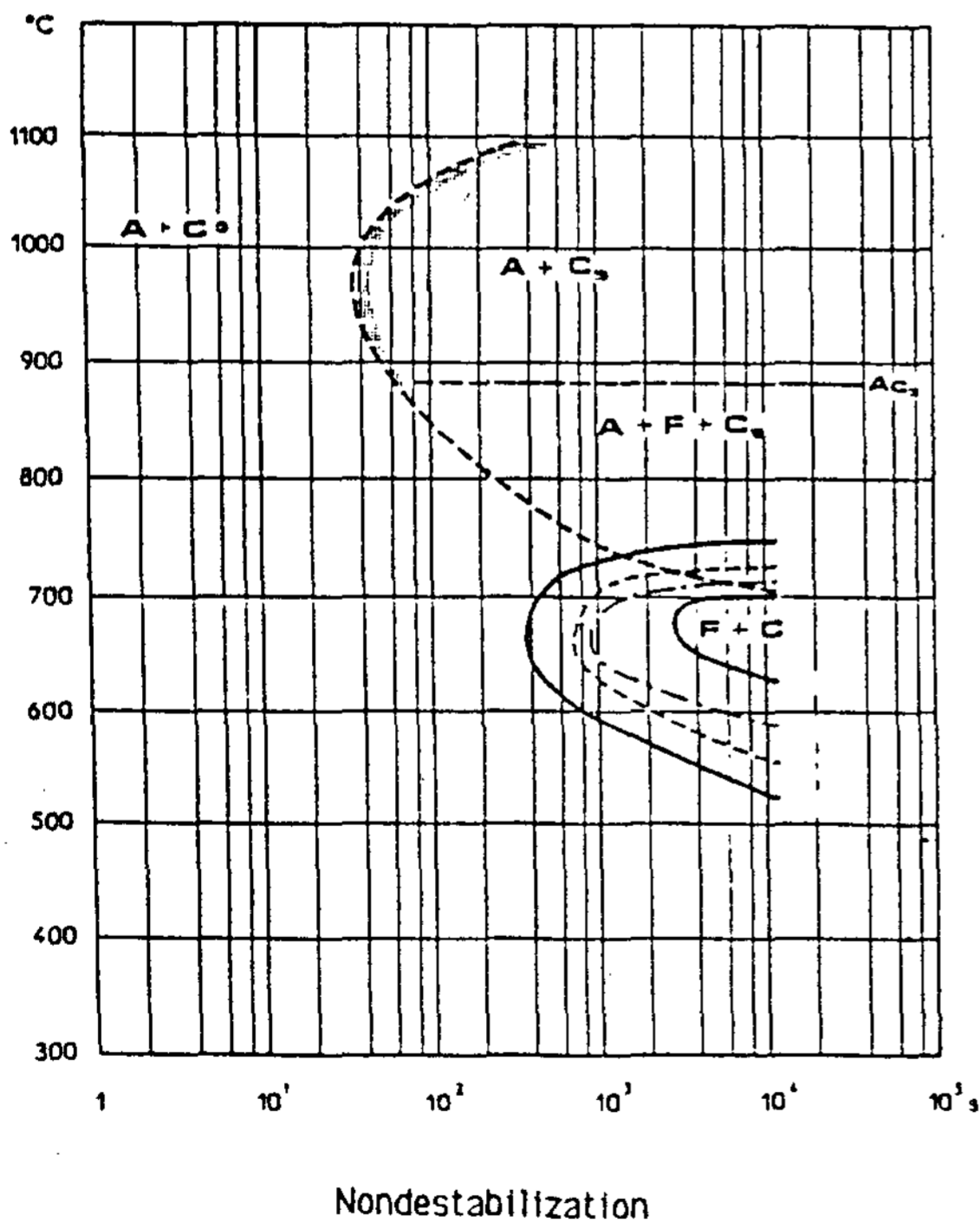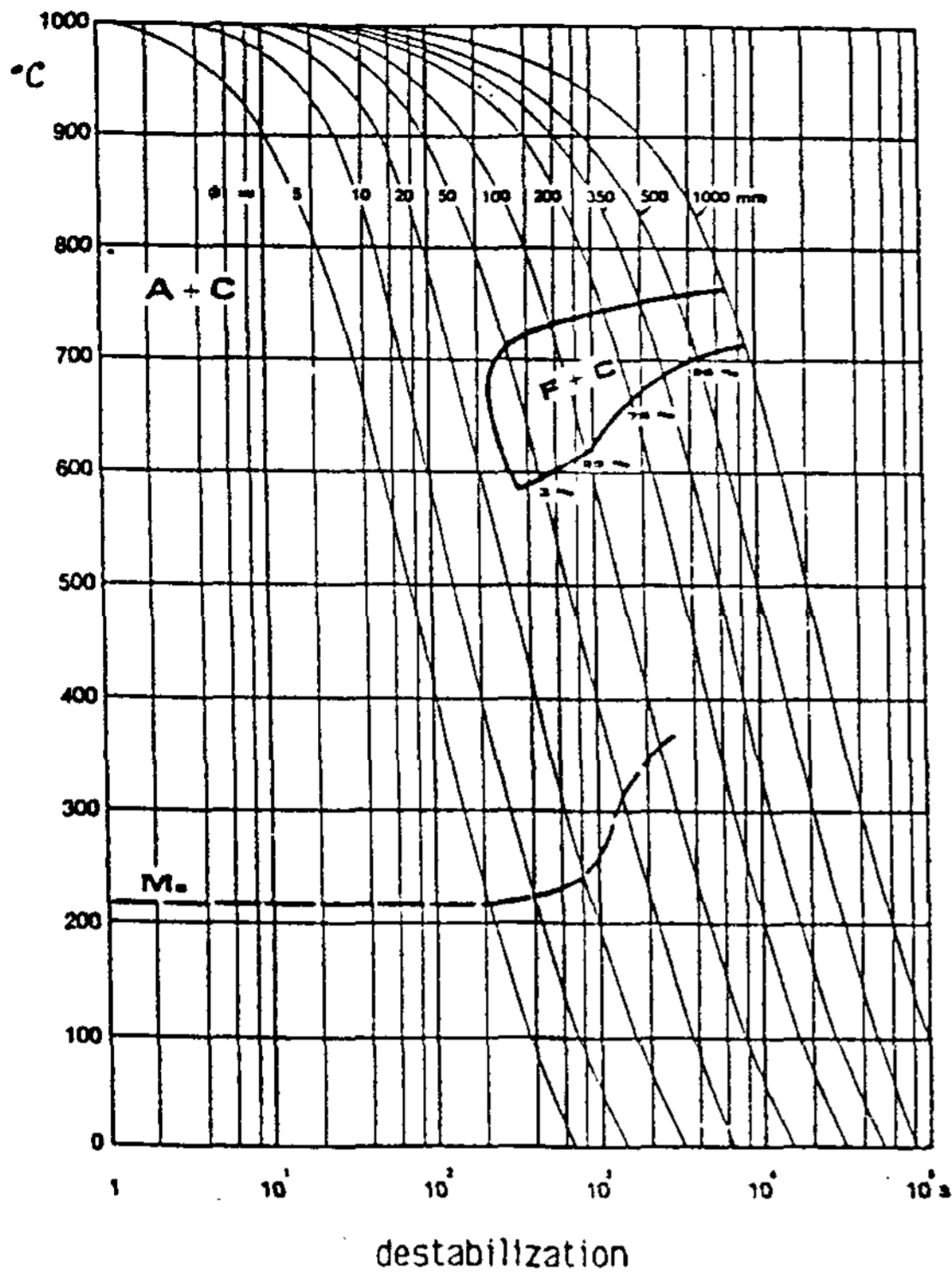
destabilization

Nondestabilization

Fig. 5. Continuous Cooling Transformation Diagrams for Nondestabilization and Destabilization in a Fe-2.67% C-14.95% Cr[15].

5 shows CCT diagram for nondestabilization and destabilization in a Fe-2.67% C-14.95% Cr alloy[7]. The composition of Figure 5 is close to the composition of the present work except the niobium content of the alloys. The thickness of samples which were used in nondestabilization and destabilization of the present work was 6.4mm and the cooling rate of the present work was higher than that of 10mm diameter of Figure 5. According to CCT diagram of Figure 5, the microstructures of the present work would consist of martensite and secondary carbides. In addition to CCT diagram of Figure 5, Maratray derived an expression for the maximum diameter which could be air hardening without forming pearlite as follows ;

$$\mathrm{Log_{10}(max\ diameter,\ mm)}=0.32+0.158Cr/C+0.385Mo$$

According to Maratray's expression, the maximum diameter being air hardened without forming pearlite in the present work is 17.7mm. It is in good agreement with the result of the present work that the microstructures consisted of martensite and secondary carbides.

Table 4 showed the hardness values of the matrix structures after destabilization. It was observed from the comparisons of Tables 2, 3 and 4 that the matrix structures which were obtained after destabilization showed higher hardness than the as-cast matrix or the matrix structures which were obtained after nondestabilization. It was believed that the hardness values of the matrix structures were increased by the formation of austenite to martensite and precipitation of secondary carbides. The larger amount of secondary carbides contributed to increase the hardness because of their higher hardness and dispersion hardening effect on the matrix structure.

On the other hand, the addition of niobium slightly increased the hardness values of the matrix structure(compare specimen no ; 2-1 to 2-4, 3-1 to 3-4). It might be believed that the amount of niobium carbide increased with an

Table 4. Hardness of the matrix of destabilized
condition

Sample number	Microhardness(HV 50G)
2-1	819
2-2	810
2-3	824
2-4	854
2-5	924
2-6	937
3-1	817
3-2	824
3-3	841
3-4	852
3-5	913
3-6	937
3-7	937

increase in the niobium content of the alloys.
The increased amount of niobium carbide in-
creased the hardness values of the matrix stru-
cture. But Guesser[11] showed the time needed
for 5% pearlite formation at 700°C as a function
of molybdenum or niobium contents in a Fe-
3% C-18% Cr alloy. He reported that additions
of up to 1% Nb allowed decreasing molybdenum
content without speeding up the pearlite forma-
tion at 700°C. But it was observed that the ad-
dition of niobium did not appear to affect the
transformation to martensite and secondary
carbides during destabilization of the present
work. And the amount of secondary carbides
and the transformation of the matrix structure
did not significantly change with an increase in
the niobium content of the alloys. The previous
work[12] showed that niobium was preferentially
partitioned to primary and eutectic niobium
carbides but it was not partitioned to austenite
and M_7C_3 carbide. It indicates that the transfor-
mation of the matrix structures would not be
affected by the addition of niobium because of
no partition to austenite. It is not clear, at pre-
sent, how the addition of niobium did affect
the hardenability of the alloys in the heat tre-
ated condition of Guesser work.

In addition, the hardness values of the matrix
structure slightly increased with an increase in
the molybdenum content of the alloy. It is in
agreement with the result of Maratray[7,13] work
even if their systems are Fe-C-Cr alloys. It has
been well recognized that the alloying elements
which promote hardness increase are those
which lower martensite start temperature(M_s)
and the hardness of alloy increases with a lo-
wer M_s temperature[13]. So it was believed from
the present work that the addition of molybd-
enum lowered M_s temperature and it increased
the hardness of the matrix structure.

On the other hand, when the pearlitic struc-
ture was austenitized(nondestabilization), the
secondary carbides were well coalesced and
uniformly distributed(Figures 1 and 2). When
an austenitic structure was reheated(destabil-
ization), the morphology of secondary carbides
was different from that of nondestabilization
(compare Figures 2 and 4). After nondestabili-
zation the pearlitic structure underwent trans-
formation to austenite and secondary carbides
and the secondary carbides so formed were
spheroids finely distributed through the matrix
(see Figure 2). Maratray[13] reported that when
an austenitic structure is reheated within a
gamma-phase field, precipitation of carbides
occurs on the glide plane of austenite, due to
the strains set up in the austenite by the diff-
erence in expansion between the primary carb-
ides and the matrix. Therefore, it was evident
that the transformation processes of the matrix
structures during nondestabilization and desta-
bilization were different and the morphology of
secondary carbides which were formed during
exposure to the austenitizing temperature was
dependent upon the prior structures.

4. Summary and Conclusions

1. In the as-cast condition, the additions of
niobium and molybdenum slightly increased the
hardness values of pearlitic or austenitic stru-

cture.

2. After nondestabilization, the microstructures consisted of austenite and secondary carbides. The samples which were pearlitic structure in the as-cast condition showed a larger amount of secondary carbides and higher hardness values than the samples which were austenitic structure in the as-cast condition. In addition, the addition of niobium slightly increased the hardness of the matrix.

3. After destabilization, the microstructures consisted of martensite and secondary carbides. The hardness of matrix was increased by the formation of austenite to martensite and precipitation of secondary carbides. In addition, the addition of niobium did not apper to affect the transformation to martensite and secondary carbides during destabilization. The amount of secondary carbides did not appear to change with an increase in the niobium content of the alloys. But the addition of niobium and molybdenum slightly increased the hardness of the matrix structure.

4. The structures of secondary carbides which were formed during exposure to the austenitizing temperature was dependent upon the prior structures.

5. Acknowledgments

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