Solubility of Carbon in 18-Percent-Chromium–10-Percent-Nickel Austenite

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A series of high-purity iron-chromium-nickel alloys, made to a base analysis of 18 percent of chromium and 10 percent of nickel, and with carbon ranging from 0.007 to 0.30 percent, was melted and solidified in vacuum. The presence or absence of carbides in these alloys after various mechanical and thermal treatments was determined by metallographic examination. The practical limit of solubility varied from less than 0.007 percent of carbon at 1,300° F to slightly more than 0.077 percent at 1,975° F, the highest temperature studied.

The presence of ferrite and/or sigma as stable phases in many of the alloys was established.

1. Introduction

The austenitic stainless steels of AISI types 302 and 304 are essentially alloys of iron with 18 percent of chromium and about 10 percent of nickel, containing relatively small amounts of carbon. Although the higher carbon content of the type 302 steel results in somewhat higher strength than is obtained in its lower carbon counterpart, type 304, it has long been recognized that this higher carbon has been the cause of lowered corrosion resistance, particularly of the intergranular variety. These steels become susceptible to intergranular corrosion if exposed to temperatures that cause the precipitation of chromium carbides. The use of type 304 stainless steel, with its 0.08 percent maximum of carbon, was based upon the premise that the lowered carbon content would render the steel more resistant to intergranular corrosion, and this point of view has been emphasized by the recent development of the type 304 ELC steels, with carbon held to a maximum limit of 0.030 percent.

Even these extra low carbon steels, however, precipitate carbides under certain conditions of time and temperature. Although such steels are definitely less susceptible to intergranular corrosion than the regular type 304, it is apparent that complete immunity to intergranular corrosion of unstabilized austenitic stainless steels can be achieved only when the carbon content is less than the limit of solid solubility. It is now generally believed that the limit of solid solubility of carbon is less than the value of 0.02 percent usually assumed.

The austenitic stainless steels are annealed with the object of obtaining a completely austenitic structure with all carbon in solid solution. To attain this end, annealing temperatures used in commercial practice are quite high, usually about 1,950 to 2,000° F. Although such high annealing temperatures are effective in causing the solution of precipitated carbides, the use of lower annealing temperatures with smaller resulting grain size is considered desirable from the viewpoint of resistance to intergranular embrittlement. As the temperature of complete solution of carbides is a function of carbon content, it appears logical to presume that the low-carbon steels may be annealed at lower temperatures than the higher carbon varieties. In the absence of definite knowledge of the carbon solubility, however, annealing temperatures must be kept quite high. It would seem that a determination of these limits would be of considerable practical as well as theoretical interest.

Despite the large amount of experimental work on the austenitic stainless steels reported in the literature, there does not appear to have been much study devoted to the determination of the limit of solubility of carbon in chromium-nickel austenite. Aborn and Bain [1] [1] note that such a determination could be made only with considerable difficulty and express a well-founded doubt that it is possible to determine the solubility of chromium carbide at temperatures below about 1,000° F. They present the results of their experimental work in the form of a curve and state that this curve represents the solubility of carbon in 18-percent-chromium–8-percent-nickel alloy, although no analyses are given. Curves are also shown by Krivobok and Grossmann [2], giving the solubility of carbon in 18-percent-chromium–8-percent-nickel and in 18-percent-chromium–12-percent-nickel austenite, and by Green [3], giving the solubility of carbon in 18-percent-chromium–9-percent-nickel austenite. Values taken from the curves of these investigators are given in table 1.

TABLE 1. *Solubility of carbon in chromium-nickel austenite according to various investigators*

| Temperature | Percentage of carbon soluble in austenite— | | | |
	18-percent-Cr–8-percent-Ni [1]	18-percent-Cr–8-percent-Ni [2]	18-percent-Cr–9-percent-Ni [3]	18-percent-Cr–12-percent-Ni [2]
° F				
1,400	<0.02	--------	--------	--------
1,500	.025	--------	--------	--------
1,600	.045	--------	--------	--------
1,700	.075	0.05	0.07	--------
1,800	.12	.10	.12	0.08
1,900	.18	.17	.17	.16
2,000	.23	.26	.24	.25
2,100	--------	.38	.32	.38
2,200	--------	--------	.41	--------

[1] Figures in brackets indicate the literature references at the end of this paper.

2. Materials and Methods of Study

The materials used in this study were all high-purity iron-nickel-chromium alloys prepared in the laboratory. The raw materials were electrolytic iron, electrolytic chromium, and Mond nickel with the following analyses:

Material	Percentage of—								
	C	Mn	P	S	Si	Cr	Ni	Fe	Cu
Iron_____	0.004	0.002	0.004	0.002	0.002	(1)	---	(2)	(3)
Chromium___	<.001	---	---	.001	---	99.4	---	<.01	<0.01
Nickel_____	.02	---	---	.002	---	------	99.9	.03	<.01

[1] Not detected.
[2] Balance.
[3] Trace.

All melts were prepared in slip-cast high-purity beryllia crucibles. The crucibles were approximately 1¾ in. in diameter by 8 in. long, and a new crucible was used for each melt. The charges were calculated on the basis of 18 percent of chromium, 10 percent of nickel, and 72 percent of iron, carbon being added in the form of high-purity graphite. Each charge weighed approximately 900 g. All heats were melted in vacuum in a small induction furnace; each melt was allowed to solidify in the crucible. It was attempted to maintain the molten metal under vacuum for a period of several hours in an effort to remove gases, but trouble was experienced because of the vaporization of chromium at low pressures. Because of this the chromium contents of the alloys were appreciably lower than the desired amount, and the ingots invariably weighed less than the charges.

The ingots were subsequently heated to 2,100° F for forging into rods of about 0.6-in. diameter, and the forged rods were cleaned by machining about 0.030 in. from the diameter. About 1 in. of the end of each rod corresponding to the bottom of the ingot was discarded, and the next inch was used for chemical and gas analyses. Millings for chemical analysis were taken from the cross section of this length. All carbon determinations were made in duplicate, and the values reported are believed to be accurate to ±0.002 percent in the lower ranges. The results of the analyses are given in table 2.

TABLE 2. *Chemical compositions of the alloys (percentage by weight)*

Alloy	C	Mn	P	S	Si	Cr	Ni	O [a]	N [a]	H [a]
3_____	0.007	<0.01	0.001	0.009	0.010	17.51	10.25	0.026	0.002	0.0003
9_____	.012	<.01	<.001	.008	.004	16.80	10.30	.003	.001	.0006
4_____	.013	<.01	<.001	.008	.003	18.26	9.90	.003	.002	.0004
2_____	.016	.042	.002	.021	.060	17.46	10.01	.023	.009	.0001
15____	.035	<.01	<.001	.010	.001	18.25	10.11	.001	.002	.0001
6_____	.077	<.01	.001	.008	.003	16.40	10.34	.001	.001	<.0001
8_____	.115	<.01	.001	.008	.002	17.08	10.31	.001	.001	.0001
5_____	.129	<.01	.001	.009	.006	17.88	10.05	<.001	.001	Nil
7_____	.134	<.01	<.001	.008	.007	16.67	10.38	.001	.001	Do.
13____	.30	<.01	<.001	.009	.001	17.39	10.37	.001	.006	.0001

[a] Determined by the vacuum-fusion method.

Alloy 2 proved to be high in both manganese and oxygen, and alloy 3 was high in oxygen. These impurities apparently had no effect upon the carbon solubility as determined in this study, nor did the variation in chromium from a low of 16.40 percent to a high of 18.26 percent.

The forged rods were annealed (½ hr at 1,975° F, water-quenched) and cleaned by grinding. A section of each rod was reduced about 40 to 50 percent in area by cold-rolling for the purpose of facilitating the precipitation of carbides during subsequent heat treatments. Samples of both the annealed and the annealed and cold-worked alloys were subsequently subjected to a temperature of 800° F for 6 weeks to precipitate carbides. Individual samples were then treated at various higher temperatures for the purpose of dissolving in the austenite all carbides in excess of the solubility limit. The schedule of temperature and time is shown in table 3.

TABLE 3. *Treatments to effect solution of carbides*

Solution temperature	Time	Solution temperature	Time
°F	Weeks	°F	Weeks
900	6	1,500	3
1,000	6	1,600	3
1,100	6	1,700	2
1,200	5	1,800	1
1,300	5	1,900	1 day
1,400	3		

Considerable thought was given to a satisfactory method of determining the limit of carbide solubility. Many methods that might give quantitative values were tried, but all proved unsatisfactory. Among the methods tried and abandoned were the following:

1. *Measurement of magnetic permeability.* Two samples of the same steel containing 0.07 percent of carbon were studied. Both samples were quenched from 1,975° F, and one was subsequently heated 2 hr at 1,200° F. Microscopic examination showed that the annealed sample had a completely austenitic structure, and that the sample heated at 1,200° F had an abundance of precipitated carbides. The magnetic permeability of both samples was about the same within the limit of experimental error.

2. *Measurement of lattice parameter.* It is known that the lattice parameter of austenite is a function of carbon content, and an attempt was made to measure the lattice parameters of the two samples mentioned above, which obviously contained different amounts of dissolved carbon. Because of the small amounts of carbon involved, however, the difference in lattice parameter was less than the accuracy of measurement.

3. *Measurement of electric resistivity.* Measurement of the electric resistivity of the two samples showed differences so small that they were within the limit of experimental error.

4. *Measurement of electrolytic-solution potential.* The measurement of electrolytic-solution potential

has been advocated as a very sensitive method of determining the boundary between a homogeneous field (in this case, austenite) and a heterogeneous field (in this case, austenite plus carbide). An exhaustive series of measurements of the electrolytic-solution potential of the two samples mentioned above was made. The results obtained were entirely too erratic to be used as a basis for determining the limits of carbon solubility.

5. *Detection of chromium carbides by X-rays.* Several samples of this same steel were annealed and then held at various temperatures to precipitate carbides. X-ray examination of these samples showed positive evidence of carbides in the samples held at the lower temperatures. Carbides could not be identified positively, however, in samples that had been held at the higher temperatures (where the amount of precipitated carbides naturally was small), even though these precipitated carbides definitely could be seen under the microscope.

6. *Determination of chromium carbide by chemical analysis.* It would seem that the amount of soluble carbon (that is, the carbon dissolved in the austenite) and insoluble carbon (the carbon precipitated as carbides) could be separated by chemical analysis. Circumstances did not permit an exploration of this experimental technique.

Following the failure of the above methods, the presence or absence of carbides in the various alloys was determined by metallographic examination only. Although the determination of the presence of precipitated carbides offered no difficulty when moderate or large amounts were present, this examination became increasingly difficult and uncertain as the amounts of carbides approached the temperatures at which complete solution took place. Moreover, the determination of whether or not carbides were present was frequently complicated by the presence of other phases, such as ferrite and sigma. Although not directly connected with the main theme of study, it was necessary to investigate the presence of ferrite and sigma in many of the specimens.

As a matter of interest, hardness measurements (Rockwell "C" and "B") were made on all samples. The data obtained could not be correlated with the solution of the carbides.

3. Results and Discussion

A major problem that arose early in the metallographic examination of the samples was the need for a positive method of differentiation between carbides, sigma, and ferrite. In many of the specimens the structures were such that a carbide etch (10-percent-sodium cyanide, used electrolytically, was adopted as a standard etch for carbides) revealed a structure that could not be definitely evaluated, and many other etchants were tried in an effort to accomplish this. In several instances metallographic examination was supplemented by X-ray examination.

It soon became apparent that definite identification of all the constituents in all the samples would increase the scope of study far beyond the limits originally contemplated, namely, the determination of the limits of carbide solubility. Even though a certain amount of study was, of necessity, devoted to the identification of other constituents, the work was mainly restricted to the determination of the presence or absence of carbides. These carbides were shown, by X-ray examination, to have parameter measurements corresponding to those reported for $Cr_{23}C_6$.

The microstructures of the 10 alloys studied, as forged and then annealed at 1,975° F, are shown in figure 1. At this temperature the carbon was in solution in all the alloys containing less than 0.115 percent of carbon. Undissolved carbides were present in this alloy (fig. 1, G) and appeared in increasingly larger amounts as the carbon content increased. As might be expected, the lower carbon alloys contained delta ferrite. At 1,975° F, this constituent was present in large amounts in the very low carbon alloys and could be detected in all alloys containing up to and including 0.077 percent of carbon (fig. 1, F).

Whether or not the alloys were cold-worked after annealing at 1,975° F and prior to holding at the precipitation temperature of 800° F appeared to have no material effect upon the temperature at which complete solution of carbides took place. However, this intermediate treatment (cold-working after annealing) greatly facilitated the precipitation of carbides at 800° F. Samples of the lower carbon alloys (less than about 0.02% of carbon), when held at 800° F for 6 weeks, usually showed but very little, if any, carbide precipitation unless cold-working had followed annealing, which indicated that 6 weeks at 800° F was not sufficiently long to secure equilibrium in the annealed alloys. As the solution temperatures were raised, precipitated carbides appeared in the lower carbon alloys which had previously been annealed only.

It was noted that this intermediate treatment frequently affected the presence of delta ferrite and sigma, particularly the latter, it being conducive to the formation of sigma phase. Sigma was found in large amounts in the lower carbon alloys, particularly in those samples that had been held in the range 1,000° to 1,300° F and frequently at higher temperatures. Its presence in some of the samples was confirmed by etching with modified Murakami's reagent (30 g of KCN, 30 g of KOH, and 60 ml of H_2O), which is reported to attack sigma only [4] and by X-ray examination. The accelerating effect of cold-work upon the formation of sigma may be observed from the relatively large amounts of sigma shown in figure 2, A and C, as compared with traces shown in figure 2, B and D. This important effect of cold-work upon the formation of sigma was shown by Jette and Foote for iron-chromium alloys [5]. The sodium cyanide etchant used for these samples reveals sigma and ferrite as well as carbides. The latter are evident in figure 2, A and C, as fine dots alined on the numerous slip planes resulting from the previous cold-working. The sigma phase is evidenced by the heavy black particles, sometimes
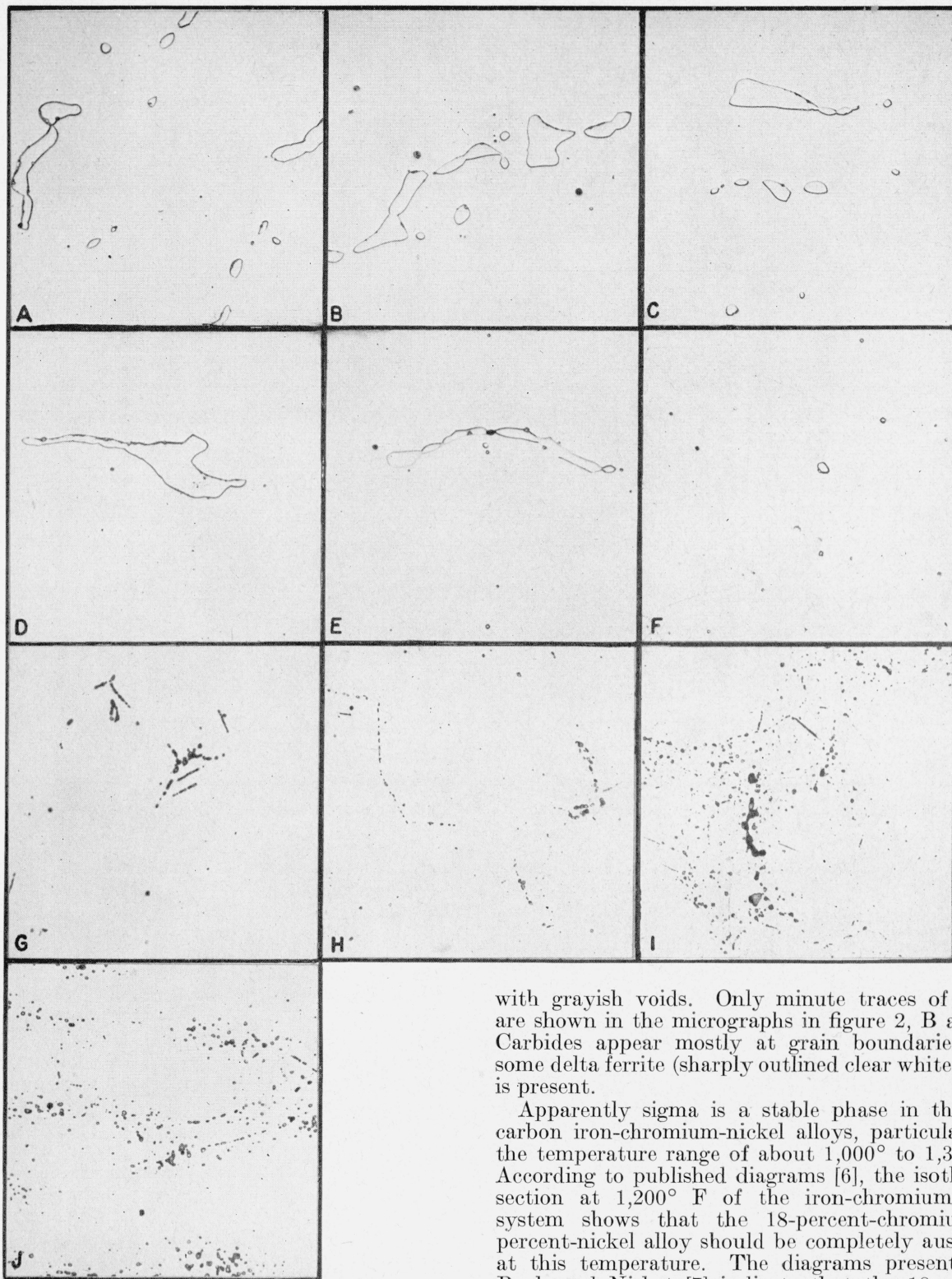
FIGURE 1. *Microstructures of the alloys as annealed at 1,975° F.*

A, Alloy 3 (0.007% C); B, alloy 9 (0.012% C); C, alloy 4 (0.013% C); D, alloy 2 (0.016% C); E, alloy 15 (0.035% C); F, alloy 6 (0.077% C); G, alloy 8 (0.115% C); H, alloy 5 (0.129% C); I, alloy 7 (0.134% C); J, alloy 13 (0.300% C). All etched electrolytically 5 minutes in a 10-percent aqueous solution of sodium cyanide. ×500.

with grayish voids. Only minute traces of sigma are shown in the micrographs in figure 2, B and D. Carbides appear mostly at grain boundaries, and some delta ferrite (sharply outlined clear white areas) is present.

Apparently sigma is a stable phase in the low-carbon iron-chromium-nickel alloys, particularly in the temperature range of about 1,000° to 1,300° F. According to published diagrams [6], the isothermal section at 1,200° F of the iron-chromium-nickel system shows that the 18-percent-chromium–10-percent-nickel alloy should be completely austenitic at this temperature. The diagrams presented by Pugh and Nisbet [7] indicate that the 18-percent-chromium–10-percent-nickel alloy should consist of alpha plus gamma at temperatures below about 1,470° F, although discussion [8] of this paper indicated that sigma could be expected to form at lower concentrations of chromium than was indicated by
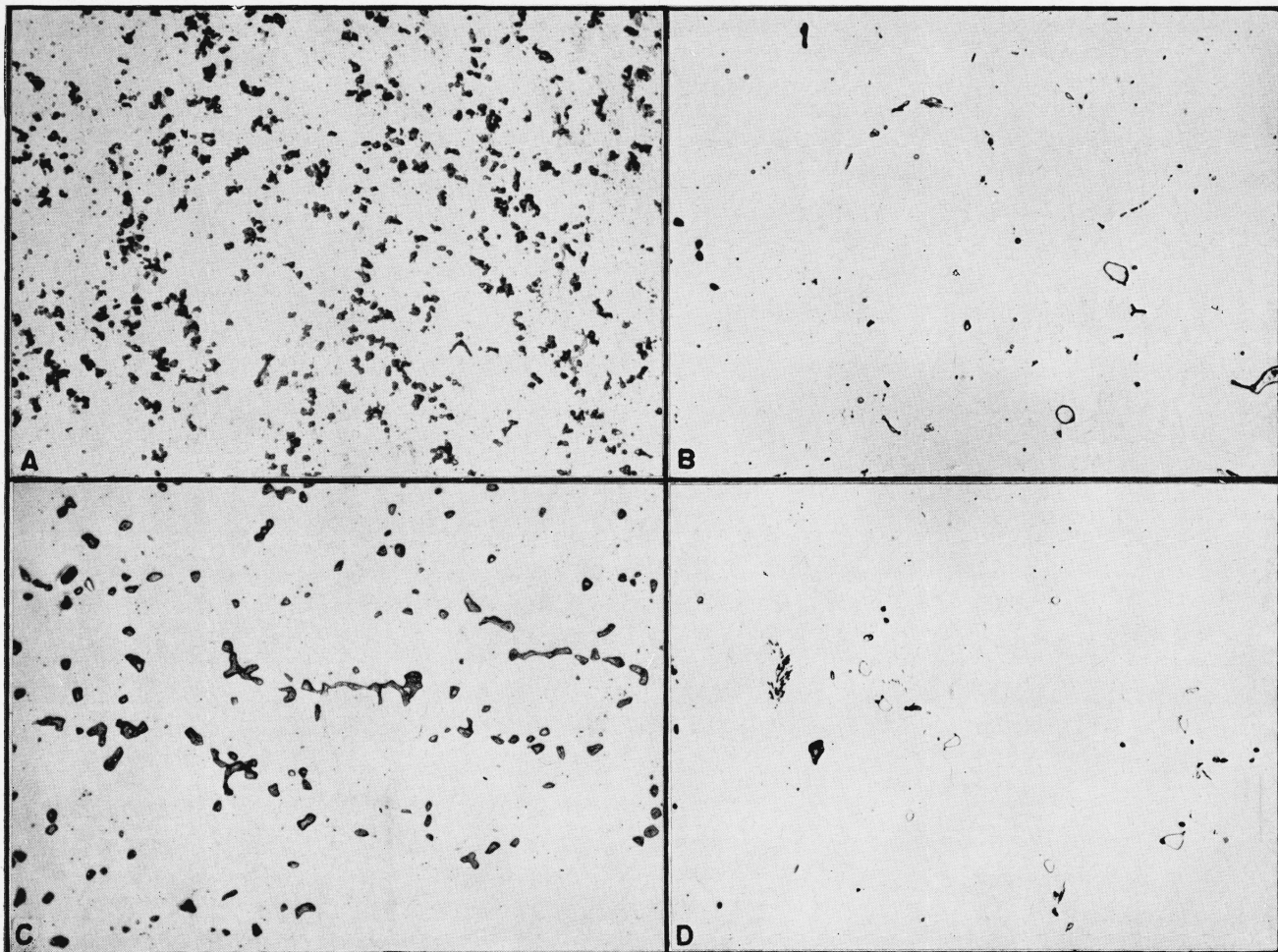
FIGURE 2. *Photomicrographs illustrating the accelerating effect of cold-working on the formation of sigma (alloy 3, 0.007 percent of carbon).*

A and C, Originally annealed and cold-worked; B and D, originally annealed; A and B, after holding at 1,000° F; C and D, after holding at 1,300° F. Etched electrolytically 2 minutes in a 10-percent aqueous solution of sodium cyanide. ×500.

Pugh and Nisbet. The work of Rees, Burns, and Cook [9] indicates that some sigma should be formed in this alloy. The iron-chromium-nickel phase diagram at 1,200° F, proposed by Thielsch [10] on the basis of the work of several investigators, indicates that the 18-percent-chromium–10-percent-nickel alloys should consist of gamma (austenite) and sigma at this temperature level. In high-purity alloys containing very small amounts of carbon, the presence of both sigma and ferrite in the range 1,000° to 1,300° F was quite definitely established in the present investigation in the alloys that had not been subjected to cold-working. It should be noted, however, that no ferrite was observed in the cold-worked low carbon alloys after 6 weeks at 1,200° F. As is shown in figure 3, the ferrite that was present in the alloys that had not been cold-worked partially transformed to sigma, and it is possible that the ferrite observed would have transformed completely to sigma had the time of exposure at 1,200° F been sufficient to attain equilibrium at that temperature.

The fact that the cold-worked alloys, solution-treated at 1,200° F, contained no ferrite lends some credence to this belief, since the intermediate cold-working assists in the attainment of structural equilibrium.

Figure 4 shows the progressive changes that took place during solution heating of alloy 15 (0.035% of carbon). The structure resulting after annealing, cold-working, and then holding at 800° F to precipitate carbides is shown in figure 4, A, and consists of ferrite and carbides (and austenite). Reheating at 900° F (fig. 4, B) caused no appreciable change, but reheating at 1,000° F (fig. 4, C) caused the formation of sigma and the virtual disappearance of ferrite. After holding at 1,100° F (fig. 4, D) considerable sigma was evident, and this constituent persisted up to 1,600° F (fig. 4, I). Carbides were still evident at this temperature, and ferrite also was present. At 1,700° F (fig. 4, J) the structure consisted essentially of austenite and ferrite, although careful metallographic examination revealed occa-
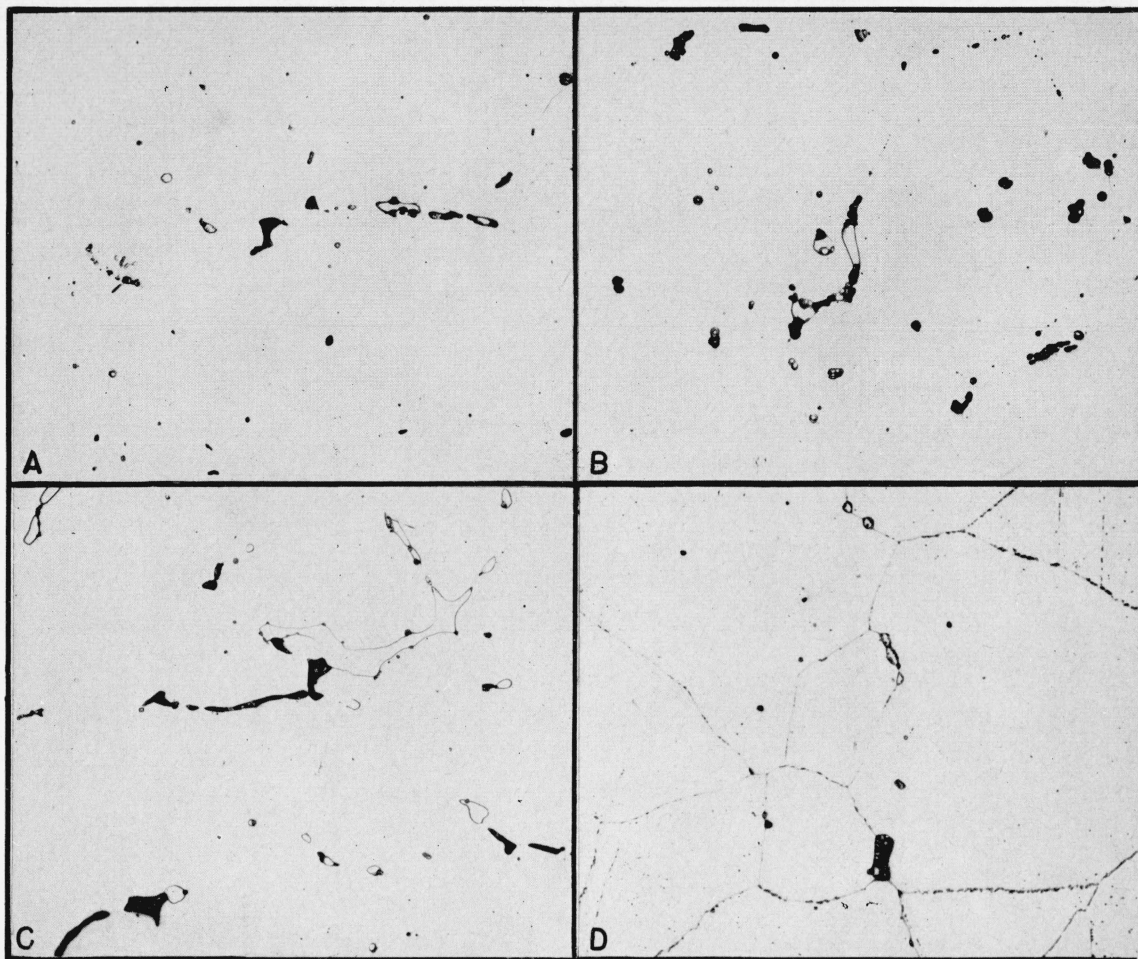
FIGURE 3. *Photomicrographs illustrating the tendency of sigma to form from ferrite.*

All alloys annealed for ½ hour at 1,975° F, held 6 weeks at 800° F, then held 5 weeks at 1,200° F. A, Alloy 3 (0.007% C); B, alloy 9 (0.012% C); C, alloy 4 (0.013% C); D, alloy 1 (0.035% C). Etched electrolytically 5 minutes in a 10-percent aqueous solution of sodium cyanide. ×500.

sional minute traces of carbides. At 1,800° and 1,900° F (fig. 4, K and L) ferrite was the only excess phase.

Figure 5 shows the changes that took place in this same alloy but without the intermediate cold-working. The structure resulting after annealing and then holding at 800° F is shown in figure 5, A, and consisted of ferrite and some slight traces of precipitated carbides in a matrix of austenite. As mentioned previously, the holding period of 6 weeks was not sufficiently long to precipitate all excess carbides at 800° F; however, carbides were readily precipitated at 900° F (fig. 5, B). At 1,000° F (fig. 5, C) sigma began to form in the ferrite areas, and essentially the same structure of carbides, ferrite, sigma, and austenite existed at 1,100° F (fig. 5, D). At 1,200° F (fig. 5, E) the structure consisted of austenite and carbides with traces of sigma. The carbides began to show evidence of coalescing at 1,300° F (fig. 5, F); sigma was also present. The photomicrograph of the sample held at 1,400° F (fig. 5, G) shows evidence of further agglomeration of carbides with sigma still persisting. At 1,500° F

(fig. 5, H) traces of ferrite were evident, and sigma was present in but small amounts; at 1,600° F (fig. 5, I) its presence was doubtful, ferrite was present in small amounts and most of the carbides had been dissolved. At 1,700° F (fig. 5, J), the structure consisted of small amounts of ferrite and doubtful traces of carbides; apparently solution of carbides was essentially complete at this temperature. At 1,800° and 1,900° F (fig. 5, K and L) the structure consisted of ferrite and austenite.

The limit of solubility of carbides in the high-purity 18-percent-chromium–10-percent-nickel alloys studied, without regard to other constituents, is shown in figure 6. Two curves are shown. The lower curve (solid) is presented as representative of the temperatures at which solution of carbides is substantially complete, that is, the temperatures above which only occasional minute traces of carbides remain. The upper curve (dashed) represents the temperatures at which all carbides have been dissolved. These curves were established on the basis of careful metallographic examination of all
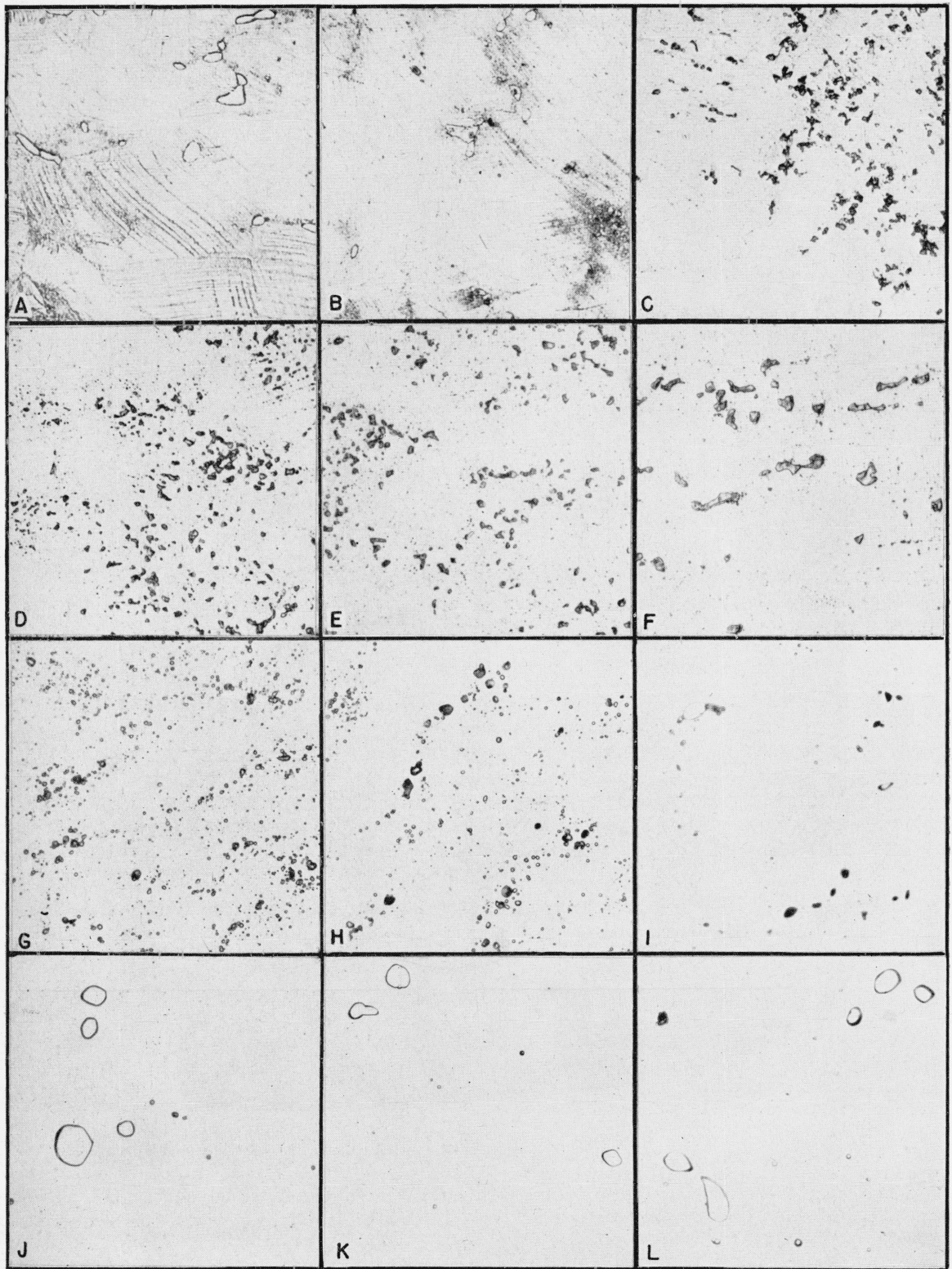
FIGURE 4. *Microstructure of alloy 15 (0.035 percent of carbon), cold-worked series, after treatment at the following temperatures.*

A, 800° F; B, 900° F; C, 1,000° F; D, 1,100° F; E, 1,200° F; F, 1,300° F; G, 1,400° F; H, 1,500° F; I, 1,600° F; J, 1,700° F; K, 1,800° F; L, 1,900° F.
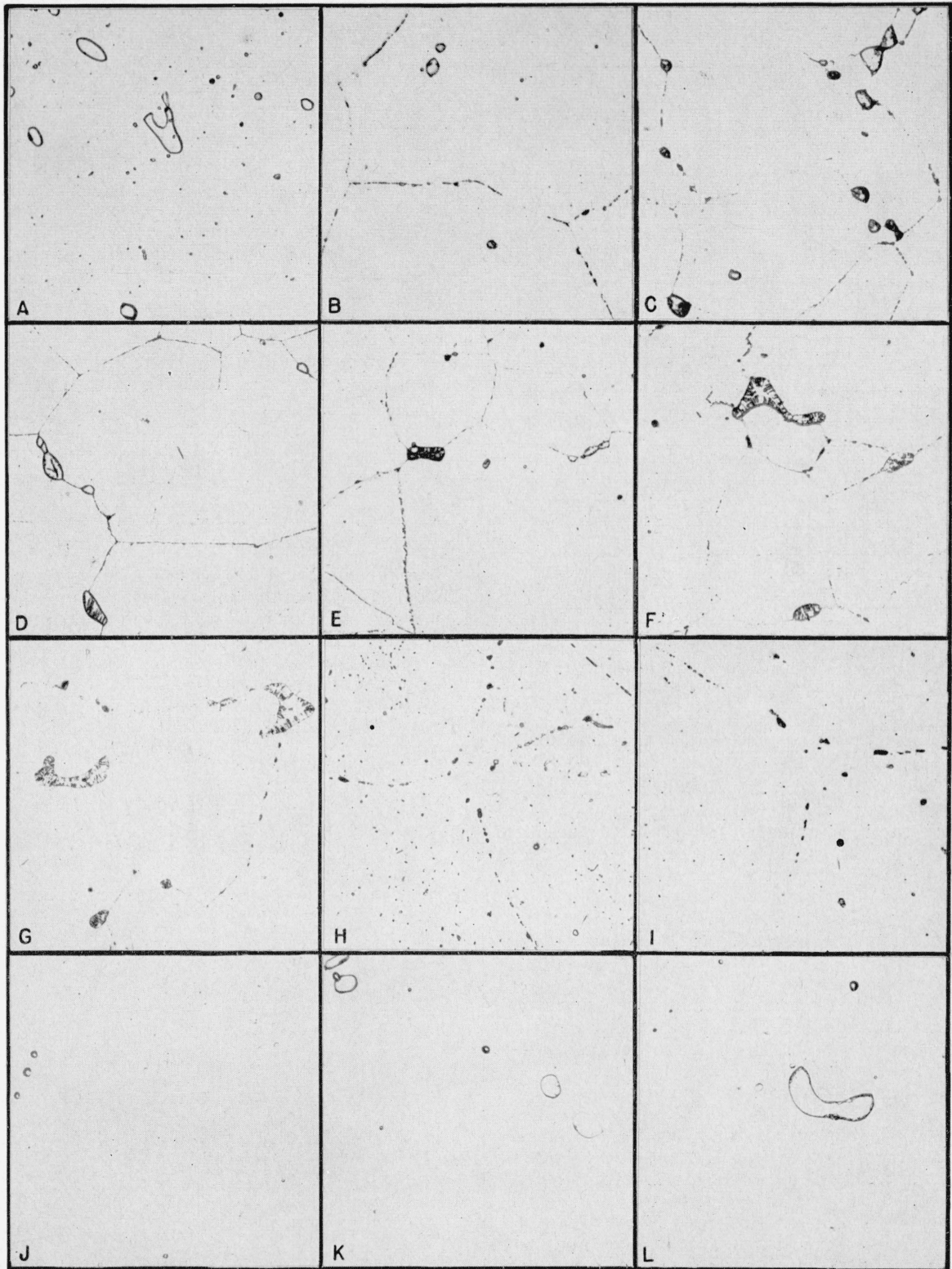All etched electrolytically 2 minutes in a 10-percent aqueous solution of sodium cyanide. ×500.

FIGURE 5.   *Microstructure of alloy 15 (0.035 percent of carbon), annealed series, after treatment at the following temperatures.*

A, 800° F; B, 900° F; C, 1,000° F; D, 1,100° F; E, 1,200° F; F, 1,300° F; G, 1,400° F; H, 1,500° F; I, 1,600° F; J, 1,700° F; K, 1,800° F; L, 1,900° F.
All etched electrolytically 3 minutes in a 10-percent aqueous solution of sodium cyanide.   ×500.
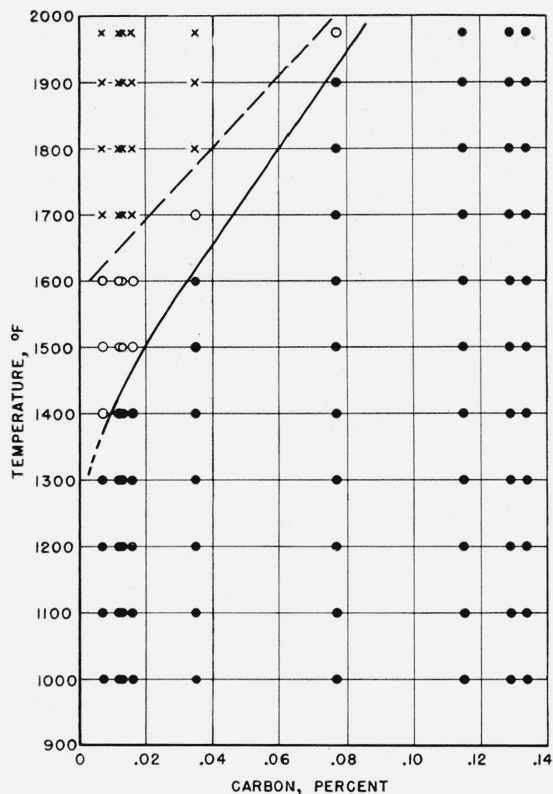
FIGURE 6. *Summary of metallographic evaluation of solubility of carbon in high-purity 18-percent-chromium–10-percent-nickel-iron alloys.*

Solid line indicates limit of substantial solubility. Dashed line indicates temperatures at which last minute traces of carbides are dissolved. ●, Carbides; ○, slight traces of carbides; ✕, no carbides.

the samples involved. At 1,900° F, the highest solution temperature used (observations obtained from the samples annealed at 1,975° F are also included in fig. 6), carbides were present in all alloys containing 0.077 present of carbon and over. At 1,300° F and below, the solubility of carbon in the base alloy was less than 0.007 percent, the lowest carbon content in the series. Minute traces of carbides could be observed in this low-carbon alloy at temperatures as high as 1,600° F. It is apparent that the solubility of carbon in the temperature range considered damaging from the viewpoint of sensitization (1,000° to 1,200° F) must be very low—certainly less than 0.007 percent.

Insofar as annealing to effect solution of carbides is concerned, it would seem that the type 304ELC steels (0.03% of carbon maximum) could be annealed at temperatures as low as 1,700° F, but that type 304 stainless (0.08% of carbon maximum) should be annealed at temperatures in excess of 1,900° F. For type 302 stainless (0.08 to 0.20% of carbon), the annealing temperatures apparently should be well over 2,000° F if effective solution of carbides is desired.

4. Summary

A metallographic study of high-purity iron-chromium-nickel alloys containing 18 percent of chromium, 10 percent of nickel, and varying amounts of carbon showed that with a carbon content of 0.007 percent (the lowest carbon content studied) solubility of carbides was substantially complete between 1,300° and 1,400° F. Complete solution of the last minute traces of carbides, however, was not effected until 1,700° F. The solubility increased as the temperature increased, and at the maximum temperature studied (1,975° F), the solubility of carbon was approximately 0.08 percent. The curve developed shows that the solubility of chromium carbide in 18-percent-chromium–10-percent-nickel austenite is appreciably lower than has been reported previously.

On the basis of the solubility curve developed, it is believed that type 304ELC stainless steel can be effectively annealed at 1,700° F but that type 304 stainless should be annealed at temperatures in excess of 1,900° F.

The existence of sigma as a stable phase in the low-carbon alloys, particularly in the range of about 1,000° to 1,300° F, was established.

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5. References

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