

# Delta Ferrite-Austenite Reactions and the Formation of Carbide, Sigma, and Chi Phases in 18 Chromium-8 Nickel-3.5 Molybdenum Steels

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Three 18 Cr-8 Ni-3.5 Mo steels of slightly different compositions were given "solution treatments" at 2,500°, 2,000°, and 1,800° F, and samples of each were reheated at 1,700°, 1,500°, and 1,200° F. Ferrite residues, remaining after dissolving the austenite in the solution-treated steels were analyzed chemically and given the reheat treatments, along with the parent steels. A metallographic study of the effect of chemical composition of the delta ferrite and austenite phases, and of the amount of delta ferrite, on the formation of carbide, sigma, and chi phases, was made. It was found that the products formed at a certain reheating temperature were influenced by the amount and composition of the delta ferrite phase present in the solution-treated steels, the amount and composition of the delta ferrite being determined by the solution-treatment temperature. Distribution ratios for Cr, Ni, Mo, and Mn in the delta ferrite and austenite phases of the solution-treated steels were 1.2, 0.5, 1.7, and 0.9, respectively.

## 1. Introduction

Commercial austenitic stainless steels are available ordinarily in the "solution-treated" condition, that is, as rapidly cooled from temperatures above 1,900° F. In this condition, AISI 316 and 317 steels frequently contain delta ferrite ( $\delta$ ) in a matrix of austenite ( $\gamma$ ). During fabrication and in service the solution-treated steels are sometimes reheated in the range of 1,200° to 1,800° F. In this temperature range, reactions occur in or between the  $\delta$  and  $\gamma$  phases that result in the formation of the microconstituents, carbide ( $M_{23}C_6$ ),  $\sigma$ , and  $\chi$  [1].<sup>1</sup> At the lower temperatures in this range the diffusion rates are extremely low, so that true chemical equilibrium is rarely, if ever, attained. Consequently, after exposure at temperatures near 1,200° F. for an arbitrarily chosen heating period, examination of the microstructure will always show an incompletely  $\delta$ - $\gamma$  reaction. The sequence of formation and the amounts formed of the carbide,  $\sigma$ , and  $\chi$  phases will be influenced by the chemical composition, relative amount, and distribution of the  $\delta$  and  $\gamma$  phases. Bowen and Hoar [2] have shown that when the reaction takes place within the  $\delta$  phase,  $\sigma$  is formed first and  $\gamma$  later. This  $\gamma$  presumably differs from the  $\gamma$  initially present in the solution-treated condition only in composition [3] and would lose its identity after diffusion had equalized the elemental concentrations. For convenience in this paper, the  $\gamma$  formed during a solution treatment will be referred to as  $\gamma_S$ , and that formed in reheating to lower temperatures as  $\gamma_R$ . A metallographic study of the effect of chemical composition of the  $\delta$  and  $\gamma$  phases, and of the amount of  $\delta$ , on the formation of carbide,  $\sigma$ , and  $\chi$  phases has been made and is reported in this paper.

## 2. Material and Heat Treatments

Three 18:8 Mo types of steel rods,  $\frac{3}{4}$  in. diameter by 4 in. long, differing slightly in chemical composition,

table 1, were used in this investigation. The "as received" condition of steel 1 was not known, but the microstructure indicated that it had been worked in the temperature range in which  $\delta$  was stable. Steels 2 and 3 were obtained through the courtesy of Mason Clogg, Armco Steel Corp., Baltimore, Md. They were from the same stock material used in the investigation, "The Development of Metallographic Methods for the Identification of the Sigma Phase in Iron-Chromium-Nickel Stainless Steels," sponsored by Sub-Committee VI, Committee A-10 American Society for Testing Materials [4]. As received, steels 2 and 3 had been heated at 2,000° F for  $\frac{1}{2}$  hour and water quenched.

In order to obtain  $\delta$  and  $\gamma$  phases of different compositions and  $\delta$  in different amounts, the three steel rods were given three solution treatments, table 2. This procedure takes advantage of the fact that for a certain steel the chemical composition of the reacting phases at equilibrium varies with temperature and that equilibrium concentrations are approximated in the solution treatment. It is not possible to vary the relative amounts of  $\delta$  and  $\gamma$  and maintain their composition constant by heat treatment because, like composition, the relative amounts vary with temperature. The  $\delta$ - $\gamma$  reaction was studied both in the presence and in the absence of the  $\gamma_S$  phase. This was done by separating the  $\delta$  phase from the solution-treated steels and reheating it in the range 1,200° to 1,700° F, along with the solution-treated steels. Table 2 lists the reheating treatments. The constitution of the reheated ferrites and solution-treated steels was then determined by a metallographic study.

TABLE 1. Chemical composition of chromium-nickel-molybdenum austenitic alloys

Steel	C	Cr	Ni	Mo	Mn	Si
1.....	0.05	17.6	7.9	3.2	0.71	0.48
2.....	.08	17.8	9.4	3.6	1.65	.49
3.....	.07	18.4	13.5	3.6	1.58	.68

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

TABLE 2. Heat treatments given steels 1, 2, and 3<sup>1</sup>

Solution treatment			Reheat treatment		
Identification	Temperature	Period	Identification	Temperature	Period
	°F	hr		°F	hr
A.....	2,500	½	K.....	1,700	340
B.....	2,000	½	L.....	1,500	500
C.....	1,800	18	M.....	1,200	500
D <sup>2</sup> .....	2,250	18			
E <sup>2</sup> .....	1,900	2			

<sup>1</sup> All specimens were water quenched from all temperatures.

<sup>2</sup> Steels 2 and 3 only.

### 3. Procedures

#### 3.1. Microscopic Examination of the Specimens

Sections of the specimens were mounted, ground, and polished by conventional procedures. The specimens were electropolished for a short period before polishing with fine alumina. The electrolyte for the electropolishing consisted of 3 parts of phosphoric acid, 3 parts of glycerol, and 4 parts of ethyl alcohol.

Among the etchants tried were weak and strong alkaline ferricyanide, sodium cyanide, and several acid reagents. It was found that aqua regia and a 10-percent sodium cyanide solution, the latter used electrolytically, were the most satisfactory for this work. Steels that contained only  $\delta$  and  $\gamma_s$  were etched with aqua regia, and those that contained carbide,  $\sigma$ , and  $\chi$  were etched with the sodium cyanide reagent. In examining the reheated steels a preliminary examination was made by a series of successive etchings. Usually 5 to 15 seconds was sufficient to reveal the carbide phase, and an additional etch for 30 seconds brought out  $\sigma$ . At this stage  $\chi$ , if present, usually could be seen faintly in the background because of relief polishing. Further etching developed  $\chi$  but overetched the  $\sigma$  and carbide phases. After this preliminary examination, the specimen was repolished and the surface etched to reveal the complete structure. In this condition the carbide and  $\sigma$  were usually overetched. It was not always possible to distinguish with certainty between  $\sigma$ ,  $\chi$ , and  $\delta$  when they were present as minute particles or as particles of the same size. In such steels a chemical separation of the microconstituents as an insoluble residue and a qualitative analysis of the separated residue by X-ray diffraction greatly aided the interpretation of the microstructure.

#### 3.2. Chemical Separation of Microconstituents from Austenite

In work done in cooperation with Subcommittee VI of ASTM Committee A-10, it was found that the microconstituents in the AISI 317 steels were relatively insoluble, with respect to the  $\gamma_s$  matrix, in solutions that contained the chlorine ion. This gave a means of concentrating the microconstituents in a manner convenient for their identification by X-ray diffraction.

The reagents that were tried included ferric chloride used electrolytically, cupric-ammonium chloride, and aqua regia. It was found that, in general,  $\delta$  was relatively insoluble in the ferric

chloride reagent but soluble in aqua regia. On this basis one of two reagents was used for the work reported in this paper: ferric chloride for steels containing  $\delta$ , and aqua regia for those containing one or more of the microconstituents—carbide,  $\sigma$ , and  $\chi$ .

In the aqua regia dissolution procedure the bulk sample was placed in approximately 100 ml of the solution and allowed to stand overnight at room temperature. In the ferric chloride procedure as used in the collection of large amounts of residue, the electrolyte consisted of 350 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  dissolved in 1 liter of water. The cell consisted of a 2-liter beaker containing 1 liter of electrolyte, with the specimen as the anode and a stainless-steel strip, 0.050 in. thick by 2 in. wide, as the cathode. The length of the specimen rod in contact with the electrolyte was approximately 3 in. The potential across the cell was controlled so as to pass a current of 1.5 amp, or about 0.03 amp/cm<sup>2</sup>; this required about 3.5 v. The voltage was not allowed to exceed 6 v. A 150-ml beaker was placed directly under the suspended specimen to catch loosened insoluble matter, although most of the residue adhered to the specimen. Small specimens were placed in a basket formed from platinum wire, and a small dish was placed beneath the basket. The electrolyte was replaced with a fresh solution after approximately 25 g of steel had been dissolved.

The residues from the aqua regia and ferric chloride treatments were separated from the solutions by centrifuging and decanting. The residues then were washed with a 50-percent nitric acid solution and then with water. When free from acid, the residues were washed from the centrifuge tubes with acetone and dried.

The ferric chloride procedure was used to separate  $\delta$  from the solution-treated steels in quantities sufficient for chemical analyses of the Cr, Ni, and Mn contents. The completeness of the separation was ascertained by X-ray diffraction. These examinations indicated that the amount of  $\gamma_s$  in the residues was less than 3 percent. This was judged from diffractometer charts by the difference in heights of the 111-peak for  $\gamma$  and the 110-peak for  $\delta$ , as compared with differences obtained from known mixtures of  $\delta$  and  $\gamma$ .

In steels suspected of containing traces of  $\delta$ , the residues were examined with a stereomicroscope for movement when a magnetized needle was passed over them. Residues that contained small amounts of  $\delta$ , as shown by X-ray diffraction, were weakly attracted by the needle, but the attraction was uniformly distributed, that is, all particles were slightly magnetic. Apparently the particles were clusters of microconstituents, some of which were ferromagnetic. In some residues there were occasional particles that were strongly attracted to the needle, and the residue as a whole showed little or no attraction. A separation was made of the strongly magnetic particles in a ferric chloride residue obtained from steel 2 after solution treatment at 2,500° F. and reheating to 1,200° F. An X-ray diffraction chart of the separated magnetic particles showed peaks corresponding to two types of oxides,  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ , and  $\text{Cr}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ . The peaks for the latter were weak.

### 3.3. Qualitative Analysis of Residues by X-ray Diffraction

The X-ray diffraction analysis of the residues were made with a Geiger-counter diffractometer and were confined to a  $2\theta$  range of  $40^\circ$  to  $65^\circ$  for diffractions of the cobalt  $K\alpha$  radiation. The peaks in the diffractometer charts nearly always could be identified as being from one or more of the  $\gamma$ ,  $\delta$ ,  $\sigma$ ,  $\chi$ , and carbide phases. The identification was made by comparing the  $2\theta$  angles for the observed peaks with the identified  $2\theta$  angles in table 3. The  $2\theta$  values are numbered in the order of their occurrence in the charts and are the averages of observed values rather than the specific values that had been reported in the literature. The corresponding  $d/n$  values were computed and listed with reported relative intensities obtained from the literature for the pure constituent. The sensitivity of detection with respect to  $\sigma$  is about 5 percent; to  $\gamma$ ,  $\delta$ , and  $\chi$ , probably about 3 percent. Phases reported as "not detected" may be considered as present in less than these amounts.

The presence of  $\delta$  and  $\gamma$  in residues separated by the ferric chloride procedure can be verified by treating the residue with aqua regia and comparing diffractometer charts obtained from the residues before and after the treatment. The treatment with aqua regia reduces the  $\delta$  and  $\gamma$  contents of the residues by dissolution. If the relative heights of peaks 7 and 9 are lowered, the presence of  $\delta$  and  $\gamma$  is indicated. This is shown in the 1AM and 1BM charts, figure 2.

## 4. Results and Discussion

### 4.1. Interpretation of Microstructure with Aid of Qualitative Analysis of Residues by X-ray Diffraction

Examples of the aid that X-ray diffraction analysis of residues gave in interpreting typical microstructures in this investigation are as follows: The small black spots in the microstructure of steel 2 after a solution treatment at  $1,800^\circ\text{F}$  (2C), figure 1, are unquestionably the carbide phase, and the large

shaded areas are  $\sigma$ . However, the smaller unshaded areas might be  $\chi$  or  $\delta$ . A diffraction chart, figure 2, of the residue obtained from 2C by the aqua regia procedure showed easily identifiable peaks for the carbide,  $\sigma$ , and  $\chi$  phases. It is unlikely that the unshaded areas in the grain boundaries are  $\delta$  because the  $\delta$  in the steel before the solution treatment was in the form of stringers. The 2C microstructure therefore was interpreted as showing  $\sigma$  in stringers,  $\chi$  as outlined areas, and carbide as black spots.

The microstructure of steel 1 after solution treatment at  $2,500^\circ\text{F}$  and reheating to  $1,200^\circ\text{F}$  (1AM, fig. 3) could not be interpreted with complete satisfaction even with the aid of an X-ray diffraction analysis of the residue. The 1AM diffraction chart (fig. 2), obtained from the residue extracted by the ferric chloride procedure, showed peaks that could be identified easily as those of the carbide and  $\sigma$  phases. The absence of  $\chi$  is indicated by the absence of peak 6, and the presence of  $\delta$  is indicated by the relative height of peak 9 not being proportional to the heights of peaks 10 and 11, such as in the 1BM ferric chloride chart. Diffraction maxima from both  $\sigma$  and  $\delta$  coincide at peak 9, table 3. From the X-ray results it can be concluded that the 1AM microstructure definitely contains carbide and  $\sigma$ , but it is possible that this 1AM microstructure also includes  $\delta$  that was not recovered in the ferric chloride extraction. In extracting  $\delta$  from steel 1 after the  $2,500^\circ\text{F}$  solution treatment, a very low yield of  $\delta$  was obtained. This indicated a relatively high solubility of  $\delta$  in the ferric chloride reagent and would account for the absence of  $\delta$  in the 1AM residue. On the basis of the foregoing results, the 1AM microstructure was interpreted as showing that the reactions were within the initial  $\delta$  sites and resulted in the formation of carbide at the  $\delta$ - $\gamma_S$  boundary and possibly within the initial  $\delta$ . These former  $\delta$  sites contained  $\sigma$ , and probably  $\gamma_R$  and undecomposed  $\delta$ . The two latter constituents, however, could not be identified.

The 2AL diffractometer chart, figure 2, obtained from the residue from steel 2 after a solution treat-

TABLE 3. X-ray diffraction data for the identification of  $\gamma$ ,  $\delta$ , carbide,  $\sigma$ , and  $\chi$  in steels 1, 2, and 3

Peak No.	Cobalt $K\alpha$ lines Degrees $2\theta$	$\gamma$		$\delta$		Carbide ( $M_{23}C_6$ )		$\sigma$		$\chi$	
		$d/n$	Intensity <sup>1</sup>	$d/n$	Intensity <sup>1</sup>	$d/n$	Intensity <sup>1</sup>	$d/n$	Intensity <sup>1</sup>	$d/n$	Intensity <sup>1</sup>
1	44.4	-----	-----	-----	-----	2.37	MS	-----	-----	2.37	M
2	46.1	-----	-----	-----	-----	-----	-----	2.28	VW	-----	-----
3	47.7	-----	-----	-----	-----	-----	-----	-----	-----	2.21	M
4	48.7	-----	-----	-----	-----	2.17	M	-----	-----	-----	-----
5	49.7	-----	-----	-----	-----	-----	-----	2.13	S	-----	-----
6	50.8	-----	-----	-----	-----	-----	-----	-----	-----	2.09	VS
7	51.3	2.07	S	-----	-----	-----	-----	2.07	W	-----	-----
8	51.8	-----	-----	-----	-----	2.05	S	-----	-----	-----	-----
9	52.5	-----	-----	2.03	S	-----	-----	2.02	W	-----	-----
10	53.7	-----	-----	-----	-----	-----	-----	1.98	M	-----	-----
11	55.1	-----	-----	-----	-----	-----	-----	1.93	S	-----	-----
12	56.6	-----	-----	-----	-----	1.89	M	1.89	M	1.89	S
13	58.0	-----	-----	-----	-----	-----	-----	1.84	VW	-----	-----
14	59.6	1.80	M	-----	-----	1.80	M	-----	-----	1.80	MS
15	60.4	-----	-----	-----	-----	1.78	W	-----	-----	-----	-----
16	61.9	-----	-----	-----	-----	-----	-----	-----	-----	1.74	M

<sup>1</sup>S, MS, M, W, and VW denote decreasing degrees in the relative heights of diffraction peaks in the diffractometer charts. No attempt was made to have these designations correspond to those recommended for the ASTM card index system.

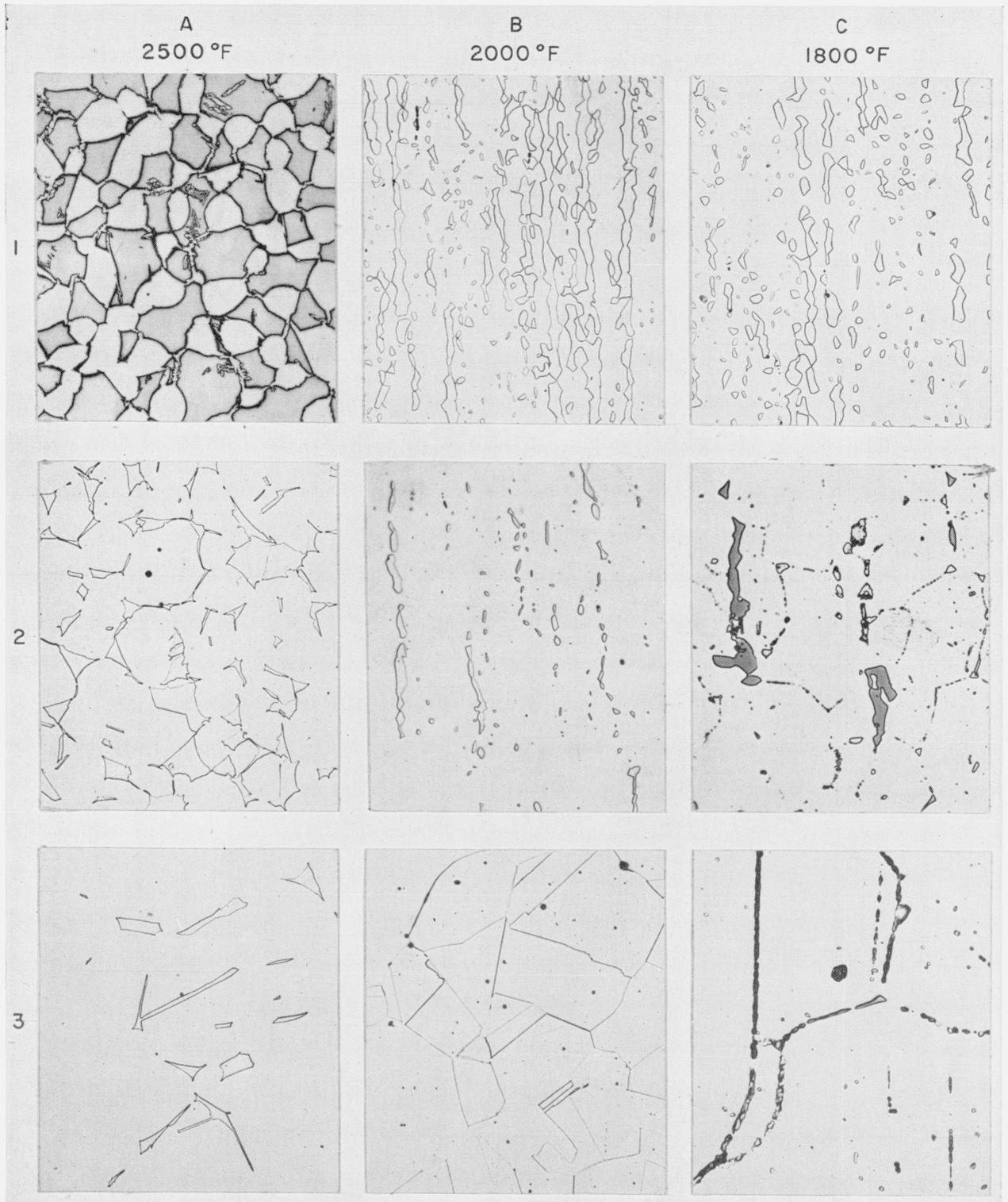


FIGURE 1. Microstructures of steels 1, 2, and 3 after solution treatments.

Numbers on the rows identify the steels; letters and temperatures on the columns identify the heat treatments. Identified constituents (matrix in all photomicrographs is  $\gamma$ ): 1A,  $\delta$  (shaded grains); 1B, 1C, 2A, 2B, and 3A,  $\delta$  (clear, outlined areas); 2C, carbide (dotted, chain-like constituent, mostly at grain boundaries),  $\sigma$  (massive, darkened areas),  $\chi$  (lighter areas, sometimes heavily attacked at outlines); 3B, none; 3C, carbide and  $\sigma$ . Magnifications: 2C,  $\times 500$ ; 3C,  $\times 1000$ ; all others  $\times 250$ . 2C and 3C were etched electrolytically with 10-percent NaCN, 1A with dilute alkaline ferricyanide, all others with aqua regia. Reduced slightly in reproduction.

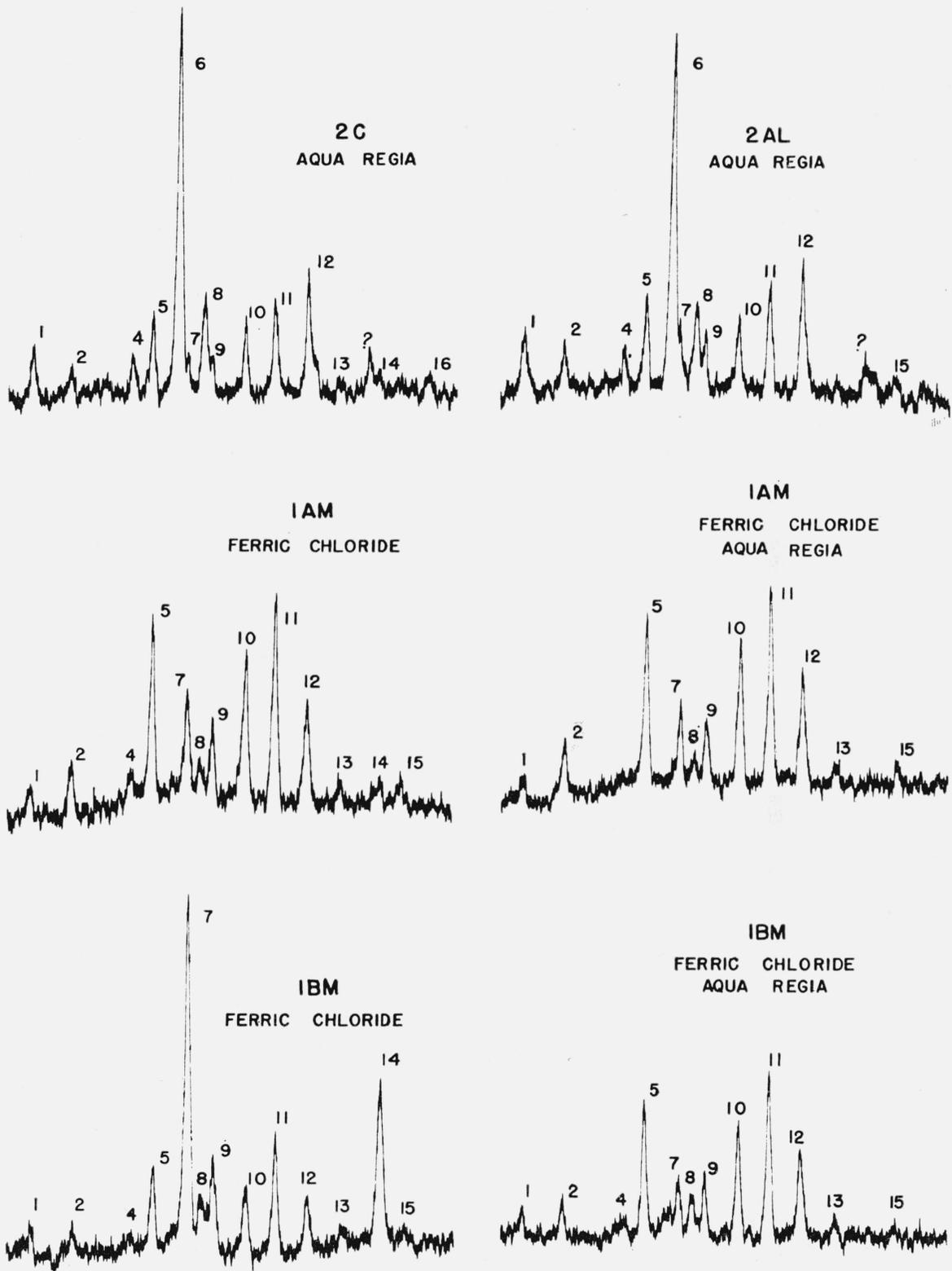


FIGURE 2. Typical X-ray diffractometer charts obtained from residues.

Charts 2C, 2AL, 1AM, and 1BM were obtained from residues separated with the ferric chloride and aqua regia reagents from steel 2 after solution treatment at 1,800° F; steel 2 after solution treatment at 2,500° F and reheating to 1,500° F; steel 1 after solution treatments at 2,500° and 2,000° F and reheating to 1,200° F, respectively. Cobalt K $\alpha$  radiation.

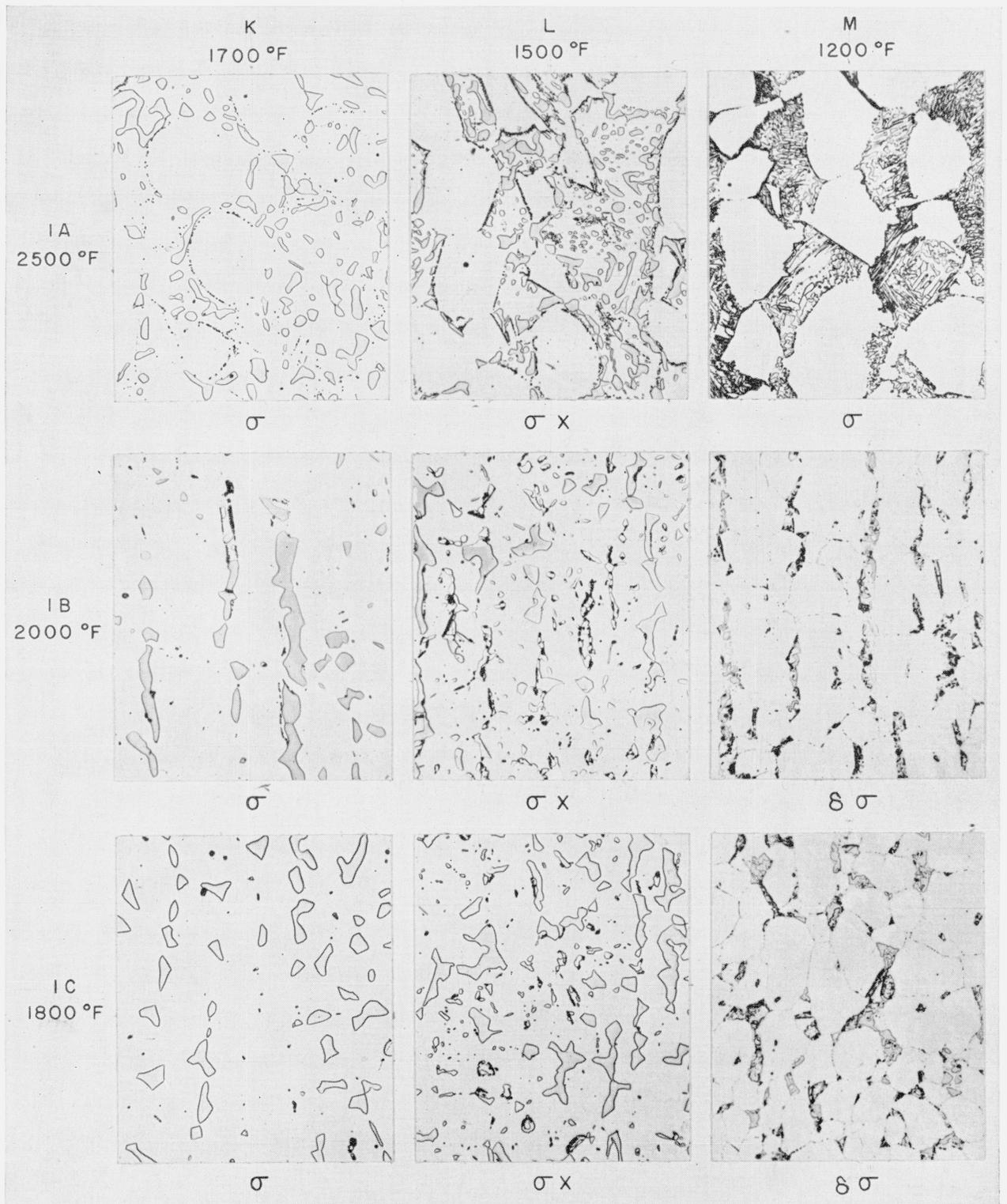


FIGURE 3. Microstructures of steel 1 after solution treatments and reheating to lower temperatures.

Numbered letters and temperatures on the rows identify the solution-treated steels; letters and temperatures on the columns identify the reheat treatments. Carbide was possibly absent in 1CK but present in the other microstructures. Identified constituents in corresponding residues are listed below each photomicrograph. Etched electrolytically in 10 percent NaCN; magnification,  $\times 500$ . Reduced slightly in reproduction.

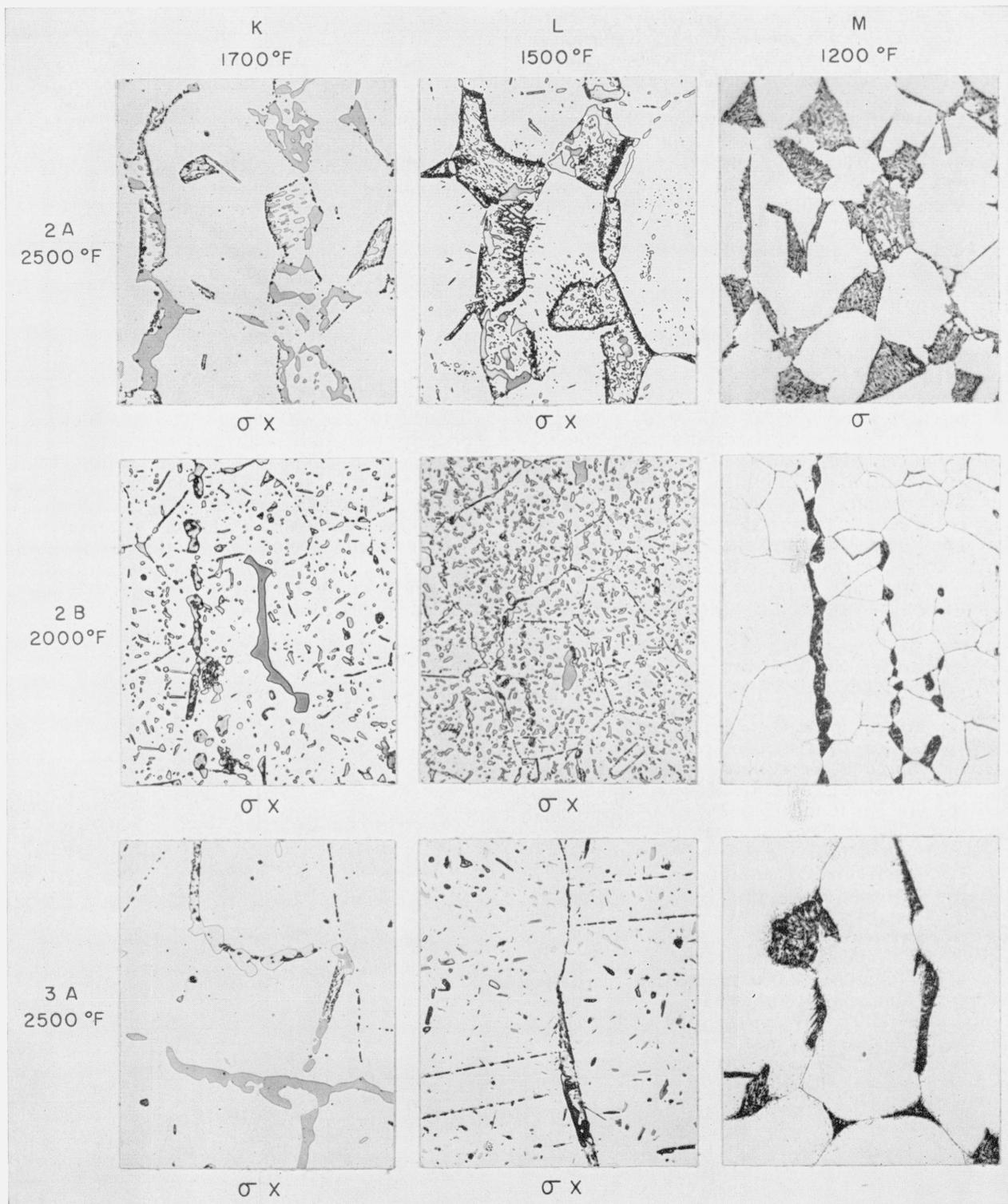


FIGURE 4. Microstructures of steels 2 and 3 after solution treatments and reheating to lower temperatures.

Numbered letters and temperatures on the rows identify the solution-treated steels; letters and temperatures on the columns identify the reheat treatments. Carbide was present in all microstructures. Identified constituents in corresponding residues are listed below each photomicrograph. Etched electrolytically in 10 percent NaCN; magnification,  $\times 500$ . Reduced slightly in reproduction.

ment at 2,500° F and reheating to 1,500° F, indicated carbide,  $\sigma$ , and  $\chi$ . On the basis of this information the 2AL microstructure, figure 4, was interpreted as showing carbides at the former  $\delta$ - $\gamma_S$  grain boundary,  $\sigma$  as large shaded areas, and  $\chi$  as small intergranular areas, not shaded. It was not always possible to distinguish between small particles of  $\sigma$  and those of  $\chi$ . The heights of peak 7 in the 1AM and 1BM charts, ferric chloride, figure 2, indicate the presence of  $\gamma$ . Diffraction maxima from  $\sigma$  and  $\gamma$  coincide at peak 7 and in the absence of  $\gamma$ , the heights of peaks 7 and 9 are about the same. This is shown in the other charts of figure 2. There is no obvious explanation for the presence of  $\gamma$  in the 1AM and 1BM residues extracted by the ferric chloride procedure. Experience has shown that the presence of  $\gamma$  is more probable in residues separated from steels that were reheated to 1,200° F than from solution-treated steels.

A successful application of the X-ray diffraction procedure described in the foregoing paragraphs depended upon having small-sized crystals, randomly oriented and intimately mixed. The experience has been that chemically separated residues satisfied these conditions. The relative solubilities of the microconstituents is dependent on the composition of the extracting reagent and of the steel, so that the procedures used for the 18:8 Mo type steels may apply only to austenitic steels containing molybdenum.

#### 4.2. Steels after Solution Treatments at 2,500°, 2,000°, and 1,800° F

It is stated in section 2 that in order to obtain  $\delta$  and  $\gamma_S$  phases of different compositions so that the  $\delta$ - $\gamma_S$  reactions could be studied, steels 1, 2, and 3 were given solution treatments at 2,500°, 2,000°, and 1,800° F. It was found that  $\delta$  was not present in all of these steels at these temperatures. The microstructures and identified constituents are shown in figure 1. The results are summarized graphically in figure 5. In order to fix the boundaries more accurately, steels 2 and 3 were examined also after solution treatments at 1,900° and 2,250° F, respectively. Microscopic examination of steel 3 after solution treatments at 2,000° and 2,250° F showed only  $\gamma_S$ . A similar range in which only the  $\gamma_S$  phase is stable apparently does not exist for steels 1 and 2. This single-phase range probably increases with a decrease in the Cr/Ni ratio. It is noteworthy that the ferrite content increases with (a) increase in temperature, or (b) with the Cr-Ni ratio. Steels 2 and 3 apparently did not contain  $\delta$  after solution treatment at 1,800° F; however, they did contain the carbide and  $\sigma$  phases. The  $\chi$  phase was detected in steel 2 but not in steel 3 at 1,800° F. Examination of the steels after reheat treatments at 1,700° and 1,500° F, figures 3 and 4, indicated that there were fields in which the  $\chi$  phase was not stable.

In order to determine the compositions of the  $\delta$  and  $\gamma_S$  phases in the solution-treated steels it was necessary to determine the relative amounts of  $\delta$  and  $\gamma_S$ . This was done microscopically by lineal

analysis according to the procedure developed by Howard and Cohen [5]. The percentages of  $\delta$  are given in figure 5. With these values, along with the Cr, Ni, Mo, and Mn contents of the separated  $\delta$  residues and of the parent steels, the compositions of the  $\gamma_S$  phase were computed, table 4. Values for the  $\delta$  and  $\gamma_S$  phases in steel 1 after solution treatment at 2,500° F are not given because the residues were contaminated with nonmetallic inclusions. This contamination was the result of a very low yield obtained in the ferric chloride separation.

The data in table 4 indicates that the  $\delta/\gamma_S$  distribution ratios of the chromium, nickel, molybdenum, and manganese contents are approximately 1.2, 0.5, 1.7, and 0.9, respectively, over these ranges of temperature and composition.

In order to know the approximate compositions of the  $\sigma$ ,  $\chi$ , and carbide phases, residues whose X-ray diffraction analysis had shown them to be composed primarily of one of these phases were analysed chemically for Cr, Ni, Mo, and Mn contents. The small amount of residue available for chemical analysis precluded determinations of the carbon and silicon contents. The results, table 5, show that the manganese contents of the carbide,  $\sigma$ , and  $\chi$  phases are approximately the same as that of the parent steels. The chromium and nickel contents of  $\sigma$  are about the same as that of  $\chi$ , but the molybdenum content is appreciably less.

TABLE 4. Chemical composition of  $\delta$  and  $\gamma_S$  after solution treatments

Steel	Solution treatment	Phase	Composition			
			Cr	Ni	Mo	Mn
	° F					
1	2,000 (B)	$\delta$ -----	20.7	5.0	4.9	0.7
		$\gamma_S$ ----	17.0	8.4	2.9	.7
	1,800 (C)	$\delta$ -----	21.3	4.5	5.3	.7
		$\gamma_S$ ----	17.0	8.4	2.9	.7
2	2,500 (A)	$\delta$ -----	19.1	5.6	5.3	1.3
		$\gamma_S$ ----	17.5	10.4	3.2	1.7
	2,000 (B)	$\delta$ -----	18.4	4.9	5.8	1.3
		$\gamma_S$ ----	17.8	9.5	3.6	1.6
3	2,500 (A)	$\delta$ -----	21.8	8.0	6.3	1.4
		$\gamma_S$ ----	18.3	13.6	3.5	1.6

<sup>1</sup> Composition computed.

TABLE 5. Chemical composition of residues approximating sigma, chi, and carbide ( $M_{23}C_6$ ) phases

Phase	Cr	Ni	Mo	Mn	Source of residue		
					Steel	Solution treatment	Reheat treatment
						° F	° F
$\sigma$ -----	27.6	3.6	11.9	0.8	1	2,000 (B)	1,700 (K)
$\chi$ -----	27.9	3.0	19.4	1.3	2	2,000 (B)	1,500 (L)
$M_{23}C_6$ -----	52.9	1.9	12.5	1.3	2	2,000 (B)	1,200 (M)

#### 4.3. Ferrite Residues after Heating at 1,700°, 1,500°, and 1,200° F

Samples of the  $\delta$  residues that were separated from the solution-treated steels were sealed in vacuum in fused-silica tubes and, simultaneously with pieces of parent steels, were given the low-temperature heat treatments listed in table 2. Both the sealed residues

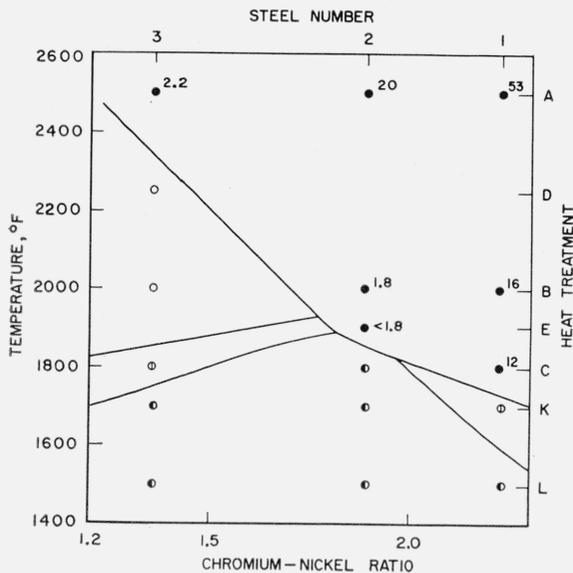


FIGURE 5. Phases in steels 1, 2, and 3 after heat treatments.

Phases identified after each heat treatment are indicated as ● for  $\delta$  and  $\gamma$ ; ○ for  $\gamma$  only; ⊕ for  $\gamma$ , carbide, and  $\sigma$ ; ⊙ for  $\gamma$ , carbide,  $\sigma$ , and  $\chi$ . Numbers adjacent to symbols are percentages of  $\delta$  as determined by lineal analysis.

and steels were quenched in water. Two of the residues were oxidized because the fused-silica tubes cracked in quenching. The residues so treated were examined for magnetic particles and then analyzed qualitatively by X-ray diffraction. The treated residues undoubtedly contained carbides in addition to the phases reported as present.

The results, table 6, show that  $\delta$  in the residues from steel 1 did not decompose completely, whereas those from steel 3 did. Excepting the residue from steel 1 after the 2,500° F solution treatment,  $\sigma$  and  $\gamma_R$  were the decomposition products. It is probable that equilibrium was attained in the 1,700° and 1,500° F reheat treatments. This means that the compositions of these residues from steel 1 were such that  $\delta$  and  $\sigma$  were mutually stable at 1,700° and 1,500° F whereas this was not the case for the residues from steel 3. This difference in stability of  $\delta$  apparently was caused by differences in composition of approximately 3 percent Ni and 1 percent Mo, see table 4. The decomposition of  $\delta$  in the residues from steel 2 apparently is more sensitive to composition. Here a

decrease of 0.7 percent of Cr, 0.7 percent of Ni, and an increase of 0.5 percent of Mo in the composition of the residue after the 2,500° F solution treatment, appeared to be sufficient to affect the stability of  $\delta$  and the kind of decomposition products.

#### 4.4. Solution-Treated Steels after Reheating to 1,700°, 1,500°, and 1,200° F

Samples of steels 1, 2, and 3 that contained the  $\delta$  phase after solution treatments at 2,500°, 2,000°, and 1,800° F, and that were reheated to 1,700°, 1,500°, and 1,200° F, were examined microscopically and their residues analysed by X-ray diffraction. The results with respect to the constituents identified in the microstructures are summarized in figures 3 and 4. In making these identifications it was assumed that the constituents in the residues were present in the microstructures, even though they could not be distinguished by etching. No attempt was made to identify or distinguish oxide inclusions. Inspection shows that the microconstituents found in the reheated steels were not always independent of the previous solution treatments. In steel 1 (fig. 3), after reheating to 1,700° F for 340 hours, the presence of the carbide phase in the sample that had been solution treated at 1,800° F (1CK) was doubtful, whereas its presence was definitely established in samples that had been solution treated at 2,500° and 2,000° F (1AK and 1BK). A similar tendency for less carbide phase after the low-temperature solution treatment also was noted in the microstructures of samples that had been reheated to 1,500° F for 500 hours, figure 3. The 1CL microstructure shows less carbide phase than the 1BL and 1AL microstructures. There is no obvious explanation for the foregoing tendency. Apparently it is affected by the amount of ferrite initially present. When the amount of the initial ferrite is but slightly greater than the  $\sigma$  that is formed, the solubility of carbon appears to be higher than when the initial ferrite is in greater excess. The work of Rosenberg and Irish [6] on high-purity alloys indicates that the solubility of carbide in  $\gamma$  at 1,700° F is of the order of 0.03 to 0.05 percent of carbon, which is slightly less than the 0.05-percent-carbon content of steel 1. In the range of 0.03 to 0.05 percent of carbon, the presence of carbides was questionable at

TABLE 6. Qualitative analysis by X-ray diffraction of ferrite residues after low temperature heat-treatments  
P, Present; ?, doubtful; and ND, not detected

Steel	Solution-treatment ° F	Heat-treatments											
		1,700° F, 340 hours				1,500° F, 500 hours				1,200° F, 500 hours			
		Unde- composed $\delta$	Decomposition products			Unde- composed $\delta$	Decomposition products			Unde- composed $\delta$	Decomposition products		
			$\gamma_R$	$\sigma$	$\chi$		$\gamma_R$	$\sigma$	$\chi$		$\gamma_R$	$\sigma$	$\chi$
1	2,500	P	P	?	ND	P	P	ND	ND	P	P	ND	ND
	2,000	P	P	P	ND	P	P	P	ND	P	P	P	ND
	1,800	P	P	P	ND	(a)	(a)	(a)	(a)	P	P	P	ND
2	2,500	ND	P	P	P	P	P	P	P	P	P	P	ND
	2,000	P	P	ND	P	(a)	(a)	(a)	(a)	P	P	ND	ND
3	2,000	ND	P	P	ND	(a)	(a)	(a)	(a)	P	P	ND	ND
	2,500	ND	P	P	ND	ND	P	P	ND	ND	P	P	ND

<sup>a</sup> Specimen damaged.

1,700° F. On the basis of their results, therefore, the presence of carbides may be expected.

Similar results in figure 4 show that for steel 2, solution treated at 2,000° F,  $\sigma$  was present as a trace after reheating to 1,200° F (2BM); however, the presence of  $\sigma$  was easily detected after solution treatment at 2,500° F and reheat treatment at 1,500° and 1,200° F (2AL and 2AM). Here again the influence of solution treatment can be traced to the amount of ferrite initially present. In addition to the effect on  $\sigma$  the 2AL and 2BL microstructures strikingly show that the amount and distribution of the reaction products have been affected by the amount of initial ferrite. The photomicrographs in figure 3 also show that  $\delta$  was not detected in steel 1 as reheated to 1,200° F after solution treatment at 2,500° F (1AM), but was present after solution treatment at 2,000° and 1,800° F (1BM and 1CM). It is probable that  $\delta$  was present in the reheated, 2,500° F solution-treated sample but could not be detected because of the solubility of undecomposed  $\delta$  in the ferric-chloride reagent. This was discussed in section 4.2.

Inspection of the microstructures of the reheated steels (figs. 3 and 4) shows that if a large amount of  $\delta$  was present initially, the reactions tended to be wholly within the  $\delta$  phase. When this is not the case the microconstituents are formed in the  $\gamma$  matrix. This tendency for the reactions to nucleate and continue within the  $\delta$  phase is illustrated by the photomicrographs in figure 4 obtained for steel 2 as reheated to 1,200° F after solution treatments at 2,500° and 2,000° F (2AM and 2BM). These microstructures show that, except for the formation of carbide in the grain boundaries, the reaction was within the  $\delta$  phase. No undecomposed  $\delta$  was identified, indicating that  $\delta$  had decomposed completely. The results in table 4 showed that the  $\delta$  in these steels did not decompose in the absence of  $\gamma_S$ ; therefore the complete decomposition of  $\delta$  in the 2AM and 2BM microstructures could not have happened without diffusion of the reacting elements from adjacent  $\gamma_S$ .

The 2BM microstructure, figure 4, is particularly interesting because of the dense mottled structure of the former ferrite, but only carbide was detected in this structure. The mottled structure probably is not entirely the result of carbide precipitation but more probably results from the etching characteristics of a transition phase [7] in the decomposition of  $\delta$  and formation of  $\sigma$  and  $\gamma_R$ . This conclusion is supported by  $\sigma$  being present in the 2AM microstructure, which shows that  $\sigma$  was stable at 1,200° F; therefore,  $\sigma$  would tend to precipitate in the 2BM microstructure. These comments also apply to the 3AM microstructure.

## 5. Summary

Three austenitic stainless steels, 18:8 Mo type, of slightly different compositions, were given three solution treatments (2,500° F, ½ hour; 2,000° F, ½ hour; and 1,800° F, 18 hours; all quenched in water), followed by reheating at three lower temper-

atures (1,700° F, 340 hours, 1,500° F, 500 hours; and 1,200° F, 500 hours) and quenching in water. The steels were examined microscopically, and the electrolytically separated residues were examined by X-ray diffraction methods.

Examination of the heat-treated specimens showed four fields of stability: a region in which  $\gamma$  was the only phase; a region in which  $\gamma$  and  $\delta$  were stable; a region in which  $\gamma$ , carbide ( $M_{23}C_6$ ) and  $\sigma$  were stable; and a region in which  $\gamma$ , carbide ( $M_{23}C_6$ ),  $\sigma$ , and  $\chi$  were stable.

The  $\delta$  was separated from the  $\gamma$  and heated at the lower temperatures along with samples of the parent steels. The chemical analyses of  $\delta$  and the computed analyses of  $\gamma$  indicated that the distribution ratios for Cr, Ni, Mo, and Mn in the  $\delta/\gamma$  phases were approximately 1.2, 0.5, 1.7, and 0.9, respectively, in the range 1,800° to 2,500° F.

Results showed that the decomposition of  $\delta$  and the kind of products that were formed were influenced by small differences in the Cr, Ni, and Mo contents.

Examination of the reheated steels showed that the amount of  $\delta$  formed in the solution treatment affected the decomposition of  $\delta$  and the kind of products formed at certain reheating temperatures. It appeared that there was a tendency for the reactions to nucleate in the  $\delta$  sites and to continue by diffusion of elements from the matrix. When the volume of decomposition products exceeded the volume of the initial  $\delta$ , the products tended to be distributed intragranularly.

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