Report No. BMI-1386
UC-25 Metallurgy and Ceramics
(TID-4500, 15th Ed.)

Contract No. W-7405-eng-92

THE SOLID SOLUBILITY AND CONSTITUTION OF YTTRIUM IN IRON-20 TO 40 w/o CHROMIUM ALLOYS

by

Martin S. Farkas
Arthur A. Bauer

October 20, 1959

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

DISCLAIMER

TABLE OF CONTENTS

THE SOLID SOLUBILITY AND CONSTITUTION OF YTTRIUM IN IRON-20 TO 40 w/o CHROMIUM ALLOYS

Martin S. Farkas and Arthur A. Bauer

The solid solubility of yttrium in iron-20 to 40 w/o chromium alloys was determined by metallographic techniques and found to be extremely small. At 1320 C, the maximum solubility is about 0.12 w/o yttrium.

Study of iron-rich alloys of the iron-yttrium system shows that the compound YFe_5 *exists. A eutectic occurs between iron and* YFe_5 *at 1257 C.*

The constitution of iron-20 to 40 w/o chromium-yttrium alloys containing less than 6 w/o yttrium was studied between 1250 and 600 C. It was found that, upon exceeding the solubility limit, YFe_5 *is formed and occurs in conjunction with alpha iron-chromium. At about 900 C and above 815 C, if more than 6 w/o yttrium is present in the iron-35 w/o chromium alloy and more than 3 w/o yttrium in iron-40 w/o chromium alloy,* YFe_4 *forms to give a three-phase field of alpha plus* YFe_5 *plus* YFe_4*. The upper yttrium limit of this phase field was not determined. At 815 C, sigma phase forms in the iron-chromium system and comes into equilibrium with* YFe_5*.*

INTRODUCTION

The study of iron-20 to 40 w/o chromium alloys containing small amounts of yttrium was prompted by discovery that yttrium improves the high-temperature oxidation resistance of these alloys. It was felt that a better understanding of the metallurgical behavior of these alloys would be forthcoming if their constitution were known.

This investigation was concerned with the determination of the solid solubility of yttrium in iron-20 to 40 w/o chromium alloys from 600 to 1320 C. In addition, the phase relations existing in the alloys containing up to 6 w/o yttrium were approximated. Study of iron-rich alloys of the iron-yttrium system was also undertaken to assist in defining ternary-phase relations.

EXPERIMENTAL PROCEDURES

Iron-yttrium and iron-chromium-yttrium alloys were arc cast. The ternary alloys were hot rolled and cold rolled, if possible. Ternary specimens were heat treated for various times at temperatures ranging from 600 to 1320 C and examined metallographically. In some cases X-ray diffraction was utilized for phase identification. Thermal analysis was employed to obtain transformation temperatures.

Alloy Preparation

Electrolytic iron, iodide chromium, and high-purity (99 per cent) yttrium were used to prepare alloys for this study.

Master alloys of iron-20, -25, -30, -35, and -40 w/o chromium were prepared by melting six to eight times in an arc furnace. These alloys were sectioned and used in preparing charges for the low-yttrium alloys used to determine solubility limits. Arc melting was utilized to provide 25 to 50-g alloy buttons. These buttons were also melted six to eight times to insure homogeneity.

Alloy compositions prepared are listed below. Subscript (n) denotes nominal composition.

Binary iron alloys containing 11, 15.3, 15.8, $20_{(n)}$, 24.2, $27_{(n)}$, 29.3, 32.1, 35.6, and 51.8 w/o yttrium

Ternary iron-20 w/o chromium alloys containing 0, 0.009, 0.01, 0.04, 0.10, 0.22, 0.29, $0.5_{(n)}$, $1_{(n)}$, $3_{(n)}$, and $6_{(n)}$ w/o yttrium

Ternary iron-25 w/o chromium alloys containing 0, $0.5_{(n)}$, $1_{(n)}$, $3_{(n)}$, and $6_{(n)}$ w/o yttrium

Ternary iron-30 w/o chromium alloys containing 0, 0.016, 0.05, 0.068, 0.10, 0.15, 0.18, 0.25, 0.73, $2_{(n)}$, $3_{(n)}$, and $6_{(n)}$ w/o yttrium

Ternary iron-35 w/o chromium alloys containing 0, $0.5_{(n)}$, $1_{(n)}$, $2_{(n)}$, 2.3, and 5.3 w/o yttrium

Ternary iron-40 w/o chromium alloys containing 0, 0.01, 0.055, 0.25, 0.39, $1_{(n)}$, $2_{(n)}$, 2.4, and 5.2 w/o yttrium.

Other iron ternaries prepared included 45 w/o chromium-2.1 w/o yttrium, 50 w/o chromium-3 w/o yttrium, 55 w/o chromium-5 w/o yttrium, 60 w/o chromium-5 w/o yttrium, 65 w/o chromium-5 w/o yttrium, and 70 w/o chromium-5 w/o yttrium. All of these compositions are nominal compositions with the exception of the 45 w/o chromium-2.1 w/o yttrium alloys.

Yttrium recovery during melting, as determined by chemical analyses of the binary alloys, was practically 100 per cent. The yttrium recovery in the iron-chromium-yttrium alloys containing less than 1 w/o yttrium varied considerably, with as little as 50 per cent or as much as 75 per cent yttrium being retained, as determined by spectrochemical analyses. Several iron-chromium-yttrium alloys containing more than 1 w/o yttrium were analyzed; these analyses show that from 79 to 90 per cent of the yttrium added to the charges was retained. Many of the alloys containing large amounts of yttrium were not analyzed and, therefore, it may be that the yttrium contents of these alloys are lower than the nominal compositions.

The iron-yttrium and iron-chromium-yttrium alloys containing 3 w/o yttrium or more were studied in the as-cast state. All other alloys were hot rolled at 1850 F and cold rolled 80 per cent.

Heat Treatment

The following time-at-temperature heat treatments were performed on the iron-chromium-yttrium alloys for the purpose of obtaining equilibrium or near-equilibrium structures for metallographic and X-ray investigations.

2 months at 600 C, water quench
3 weeks at 700 C, water quench
10 days at 900 C, water quench
4 hr at 1100 C, water quench
3 hr at 1250 C, water quench
3 hr at 1320 C, water quench.

The 600 and 700 C heat treatments were carried out in air. Heating at 900 and 1100 C was performed in a vacuum furnace. The 1250 and 1320 C heat treatments were performed in argon-flushed and -filled quartz tubes. Quenching of the latter was accomplished by breaking the quartz tubes and allowing the specimens to fall into water.

Thermal Analysis

Time-temperature thermal analysis was performed. Specimens were prepared for thermal analysis by sandwiching the bead of a platinum-platinum-10 w/o rhodium thermocouple between two small samples and spot welding. The thermocouple assembly was placed in a small vacuum-induction furnace and heated at approximately 400 C per min while recording the heating curve. Phase transformations were indicated by changes in slope of the heating curve. Although the heating rate was high, only a small temperature gradient existed in the specimen because of its small size. Also since many of the inflections or "arrests" obtained were reproducible, the high heating rate did not cause appreciable superheating.

In the case of the iron-20 w/o chromium-yttrium alloys, inverse-rate charts derived from the time-temperature curves were used to detect the transformation temperatures.

Metallography

Heat-treated specimens were mounted either in Bakelite or Kold-Weld and wet ground through 600-grit paper. The samples were polished on Forstmann cloth with diamond abrasive using kerosene as the lubricant.

The iron-yttrium alloys were etched with either nital or picral. Iron-chromium-yttrium alloys were electrolytically etched in a solution containing 10 g of oxalic acid in 100 cm^3 of water, using 6 to 10 v.

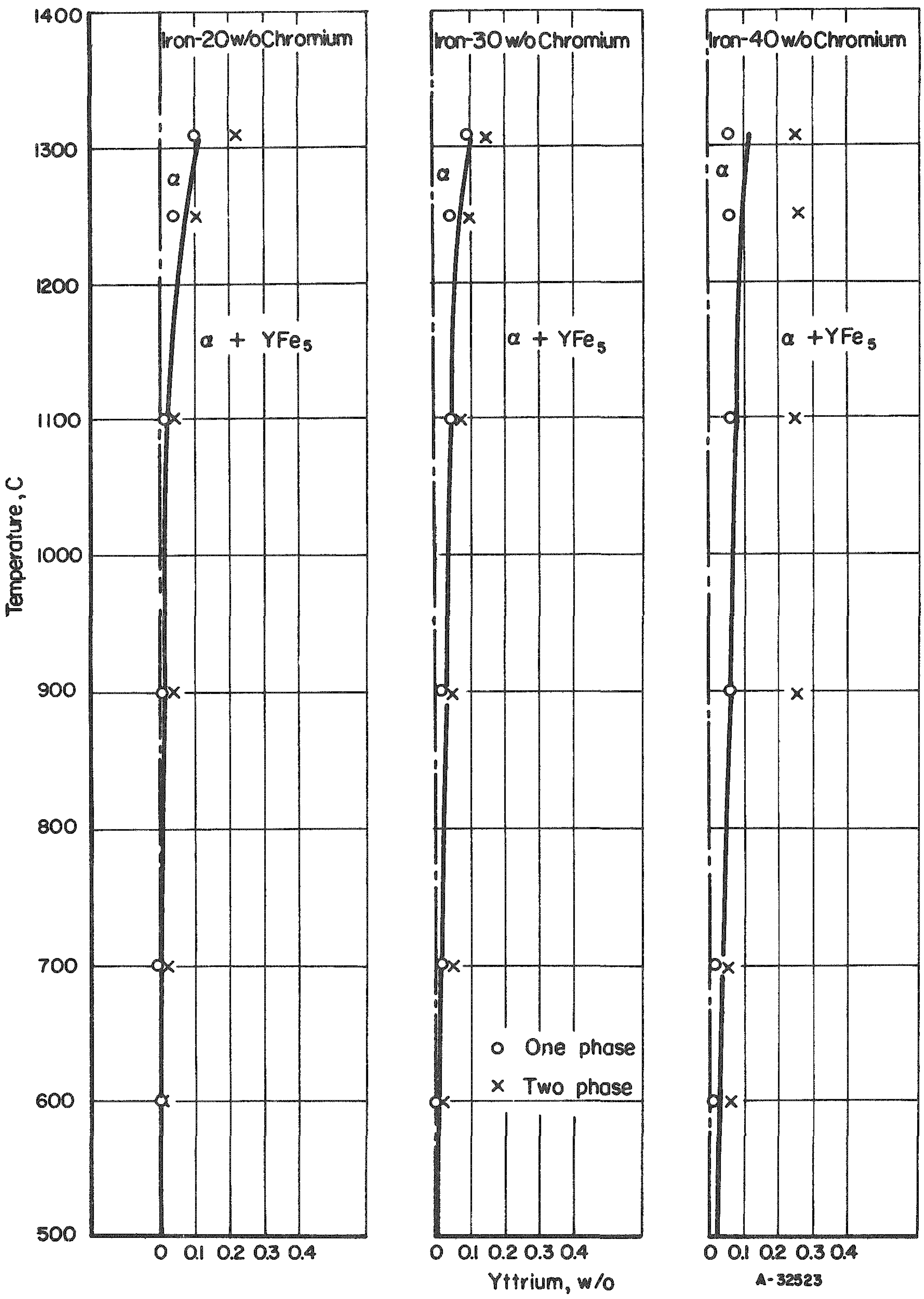


FIGURE 1. SOLUBILITY OF YTTRIUM IN IRON-20, -30, AND -40 w/o CHROMIUM

X-Ray Diffraction Examination

Metallographic specimens were used to provide X-ray samples. Generally, sliver samples of conical shape were used for examination; however, brittle specimens were examined as chips.

Modified aqua regia was used as an etchant. A 57.3-mm Debye camera was utilized to obtain X-ray photograms.

EXPERIMENTAL RESULTS AND DISCUSSION

The solid solubility of yttrium in iron-20, -30, and -40 w/o chromium alloys, from 600 to 1320 C, is indicated in Figure 1. The constitution of the iron-rich alloys of the iron-yttrium system was studied, the results are presented in Figure 2.

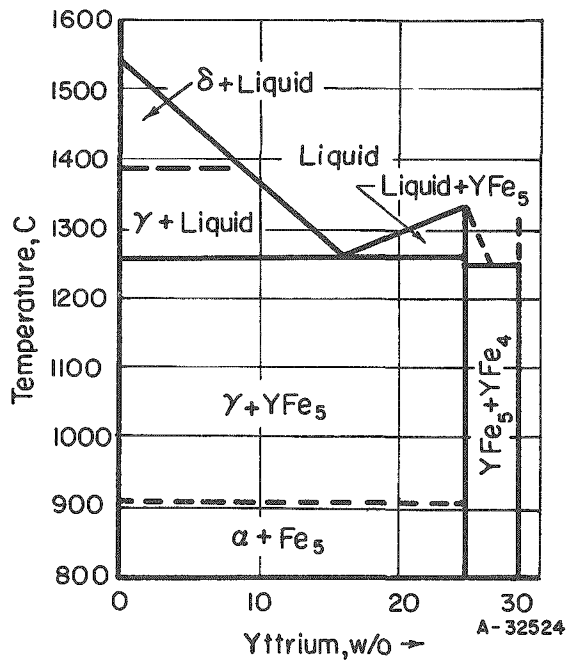


FIGURE 2. TENTATIVE PHASE RELATIONS FOR THE IRON-RICH ALLOYS OF THE IRON-YTTRIUM SYSTEM

The phase relations existing in iron-20 to -40 w/o chromium-yttrium alloys are presented in Figure 3.

Solubility Limits

The solid solubility of yttrium in iron-20, -30, and -40 w/o chromium, as determined by metallographic methods, is plotted in Figure 1. The solubility limit is placed between data points which indicate compositions of specimens between which a change from one phase to two phases is encountered.

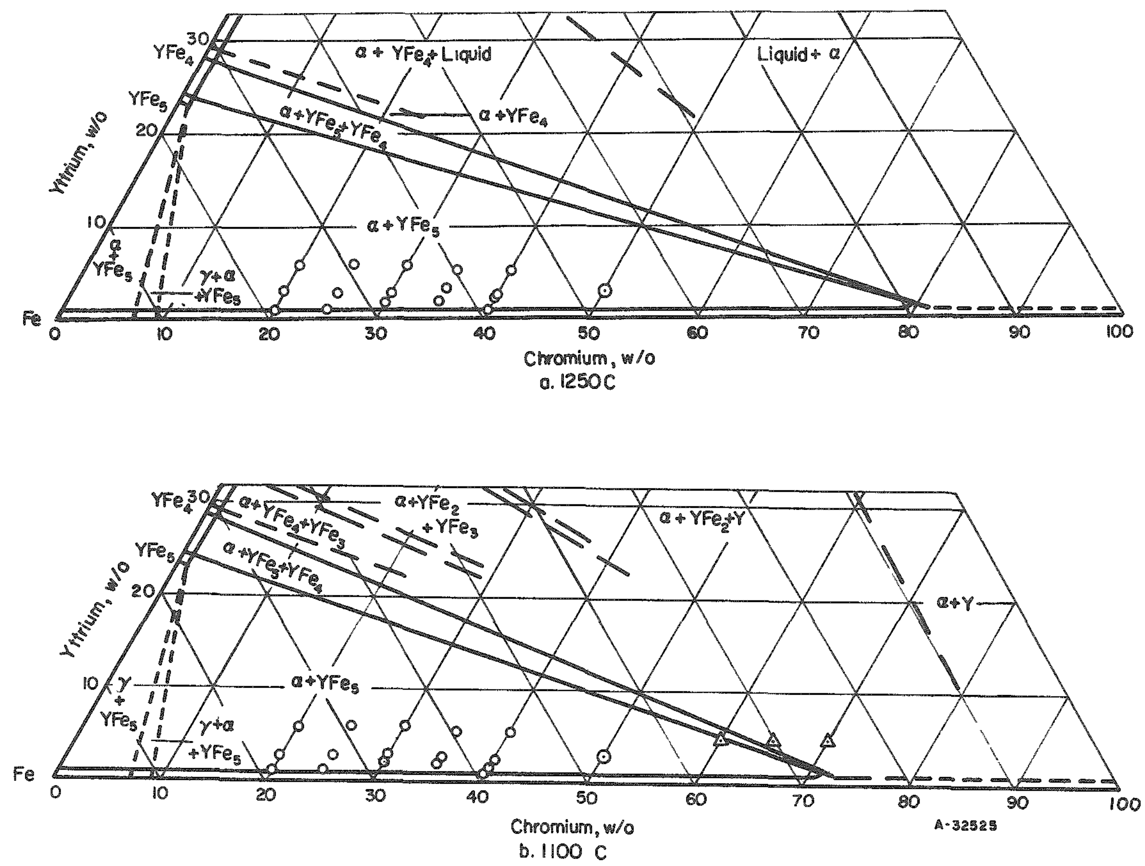


FIGURE 3. TENTATIVE PHASE RELATIONS EXISTING IN THE IRON-CHROMIUM-YTTRIUM SYSTEM

α = alpha iron-chromium
γ = gamma iron-chromium
σ = sigma

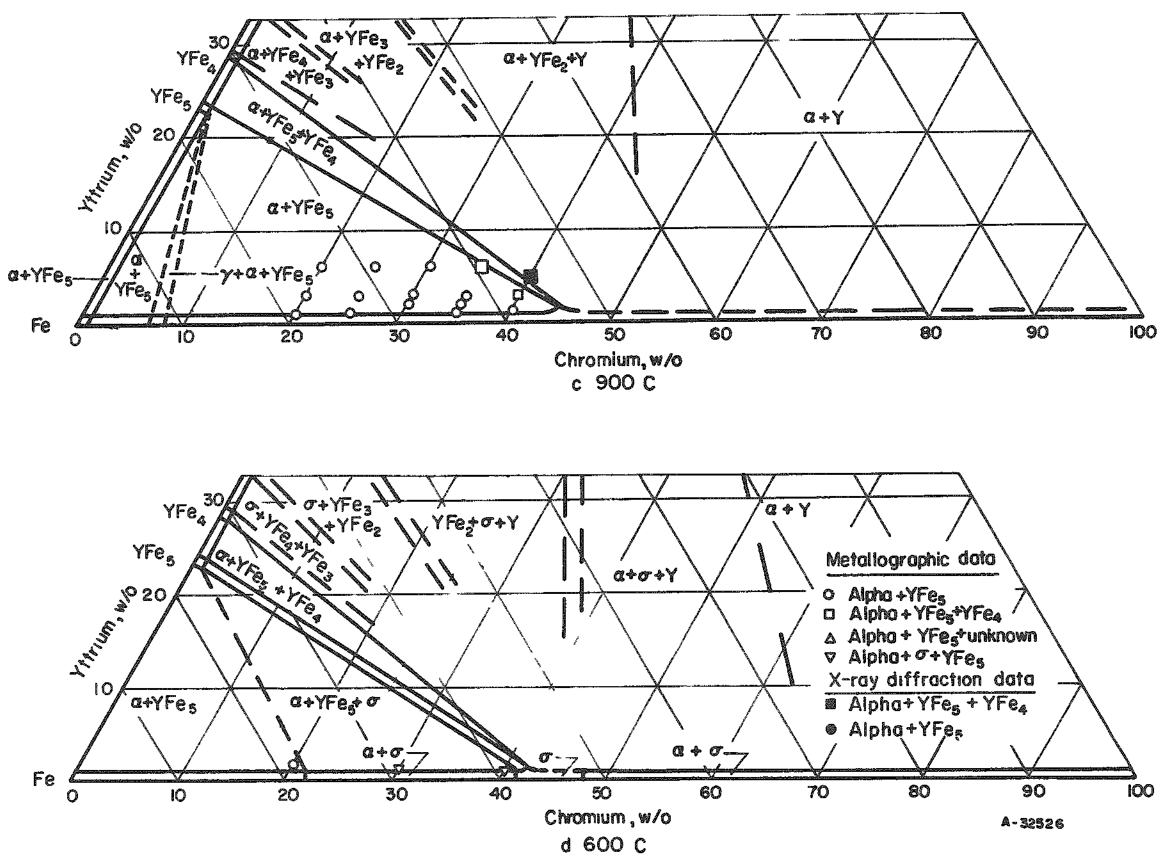


FIGURE 5. (CONTINUED)

At 1320, 1250, and 1100 C the solubilities were ascertained by comparison of samples, of the same chromium content and heat treatment, containing increasing amounts of yttrium. When YFe_5 appeared, the solubility limit was exceeded. (See the section of this report entitled "The Binary System Iron-Yttrium".) Figures 4a, b, c, and d illustrate samples of iron-30 w/o chromium and iron-30 w/o chromium-0.05, -0.10, and -0.15 w/o yttrium, respectively. These alloys were water quenched from 1250 C. It is evident that between 0.05 w/o yttrium (Figure 4b) and 0.10 yttrium (Figure 4c) the solubility limit was exceeded. The 0.15 w/o yttrium alloy (Figure 4d) shows the second phase more clearly than the lower yttrium alloys, and proves that the increasing yttrium concentration is responsible for the second phase and not impurity content.

Solubility determinations at 900 C and below were more difficult since very small amounts of YFe_5 had to be identified in the presence of background impurities. Inasmuch as the presence of YFe_5 cannot be determined unless an etchant is used, the following method was utilized. The series of alloys being used for solubility studies were examined in the as-polished condition, and photomicrographs of representative areas were taken. The alloys were then etched lightly and again examined and photographed. If a significant increase in second phase was noted in the etched sample as compared to the as-polished photomicrograph, the presence of YFe_5 was considered established. In addition, a comparison was made of etched samples of increasing yttrium content to aid in establishing the low-temperature solubility limits. Figure 5 shows an iron-30 w/o chromium-0.05 w/o yttrium alloy, quenched from 700 C, as polished and as etched, respectively. It is evident that the YFe_5 phase is present and that the solubility limit had been exceeded in this alloy.

Lattice-parameter measurements of iron-30 w/o chromium-yttrium alloys quenched from 1250 C failed to show lattice expansion of the alpha phase. Since solid solubility of yttrium in alpha iron-chromium would be accompanied by a lattice expansion, it is concluded that yttrium solubility, in this case, is too low to cause a detectable change in lattice parameter. Therefore, the lattice-parameter method is not an appropriate means for measuring solubility in this case.

As can be seen from the data presented in Figure 1, the solubility of yttrium in iron-20, -30, and -40 w/o chromium alloys is extremely low. Even near the melting point of YFe_5 (approximately 1320 C in ternary alloys) the solubility is at most about 0.15 w/o yttrium. These solubility determinations are in agreement with another investigation(1) in which the solubility of yttrium in iron-25 w/o chromium at 1260 C was found to be slightly over 0.07 w/o; and the solubility of yttrium in iron-50 w/o chromium at 1260 C was determined as approximately 0.09 w/o.

A slight increase in the solid solubility of yttrium in alpha iron-chromium is indicated as the chromium content increases particularly at low temperatures. This trend can be seen in Figure 1. The solubility of yttrium in pure iron is not known. However, it is certainly quite low because of the large difference in atomic diameters (yttrium, 3.60 A and iron, 2.48 A), and the large electronegativity difference, as indicated by the tendency to form YFe_5. The solid solubility of yttrium in chromium is about 0.1 w/o from room temperature to 1260 C(1). The solubility of yttrium in chromium is probably greater than that of yttrium in iron because the chromium-yttrium system does not exhibit compound formation and the atomic diameter of chromium is similar to that of iron (chromium, 2.50 A). Thus an increase of yttrium solubility with the chromium content of alpha iron-chromium solution is expected.

(1) References are at end of text.

250X RM11906

a. Iron-30 w/o Chromium
Structure is alpha iron-chromium.

250X RM11907

b. Iron-30 w/o Chromium-0.05 w/o Yttrium
Structure is alpha iron-chromium.

250X RM11908

c. Iron-30 w/o Chromium-0.10 w/o Yttrium
Structure is alpha iron-chromium plus YFe_5.

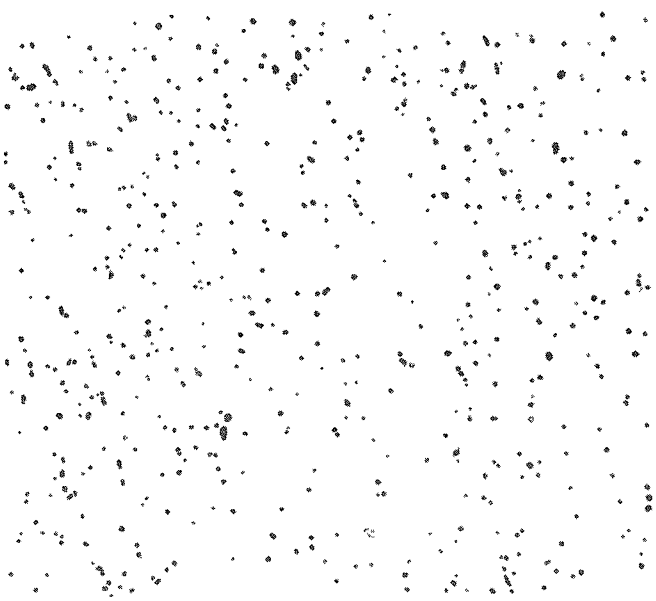
250X RM11909

d. Iron-30 w/o Chromium-0.15 w/o Yttrium
Structure is alpha iron-chromium plus YFe_5.

FIGURE 4. IRON-30 w/o CHROMIUM AND IRON-30 w/o CHROMIUM-0.05, -0.10, and -0.15 w/o YTTRIUM ALLOYS HELD 3 HOURS AT 1250 C AND WATER QUENCHED

250X N60363

As Polished



250X N60368

Etched in 10 Per Cent Oxalic Acid, 6 Volts

FIGURE 5. IRON-30 w/o CHROMIUM-0.05 w/o YTTRIUM ALLOY QUENCHED FROM 700 C

Increase in second phase in etched specimen indicates presence of YFe_5.

The Binary System Iron-Yttrium

The iron-yttrium system has been partially resolved by another investigator[2]. Results of studies conducted in this investigation of the iron-rich iron-yttrium alloys are in essential agreement with the previous study, and are presented in Figure 2. However, one major difference is apparent, the composition of the highest iron compound previously was reported as YFe_9[2], whereas in this investigation YFe_5 was found instead of YFe_9. The existence of YFe_5 was first suspected, because an analogous system, the cerium-iron system, contains the compound $CeFe_5$. Evidence to support this finding is reported in this section along with other information obtained on these alloys.

Thermal analyses of the iron-yttrium alloys are presented in Table 1. Because some of the thermal arrests obtained in the binary alloys were not always reproducible, the temperatures reported represent thermal arrests obtained in at least three separate determinations.

TABLE 1. THERMAL ANALYSES OF IRON-YTTRIUM ALLOYS

Composition (Balance Iron), w/o	Temperatures of Reproducible Thermal Arrests, C	
11 yttrium	1258	1346
15.3 yttrium	1260	1339
20 yttrium(a)	1254	--
24.2 yttrium	1252	1332
27 yttrium(a)	1250	1307
51.8 yttrium	910	1200-1237

(a) Nominal composition.

The temperature of the iron-YFe_5 eutectic is set at 1257 C on the basis of data obtained from the iron-11, -15.3, and -20 w/o yttrium alloys. It is in excellent agreement with data reported earlier[2]. No thermal arrests associated with the alpha-to-gamma iron transformation were identified, and, therefore, this transus is shown as a dotted line in Figure 2. The temperature which YFe_5 melts, as indicated by thermal analysis of the iron-24.2 w/o yttrium alloy is approximately 1332 C.

Microstructures exhibited by the iron-yttrium alloys are shown in Figure 6. The iron-11 w/o yttrium alloy, as cast, is shown in Figure 6a; the white phase is YFe_5 and the light-gray particles are alpha iron. Small amounts of a dark constituent are also seen, but these have not been identified. Figure 6b depicts the as-cast structure of iron-15.8 w/o yttrium alloy. The herringbone-type pattern indicates that the iron-YFe_5 eutectic has been approximated. Since this alloy is near the YFe_9 (15 w/o yttrium) composition and is undoubtedly two phase, it is evident that YFe_9 is not formed directly from the melt. This alloy when heated to 1400 C and slowly cooled is pictured in

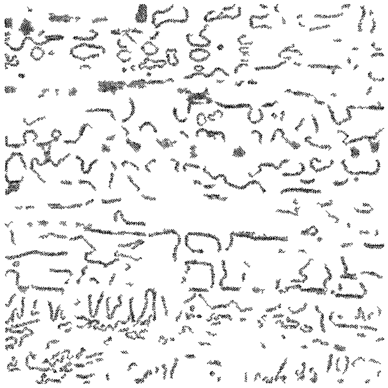
Figure 6c. The alpha iron has agglomerated and spheroidized. The YFe_5 matrix shows cracks which have not propagated through the more ductile alpha-iron particles. Figure 6d exhibits the microstructure of the iron-20 w/o yttrium alloy. The white matrix phase is YFe_5; it is surrounded by what is apparently a eutectic of alpha iron and YFe_5. The iron-20 w/o yttrium alloy is the last alloy prepared in the iron-yttrium series that exhibited alpha iron in its microstructure. An iron-24.2 w/o yttrium alloy, Figure 6e, contains YFe_5 and YFe_4 (as identified by X-ray diffraction). Although this alloy is apparently short of the stoichiometric YFe_5 composition, by 0.1 w/o yttrium the presence of YFe_4 indicates that the yttrium content is somewhat greater than the amount needed to form YFe_5 (24.3 w/o yttrium). This indicates either a slight error in yttrium analysis or that YFe_5 exists and is most stable at an yttrium content slightly lower than the theoretically correct stoichiometric composition. This is not a pure single-phase alloy as would be expected; however, because of the narrow range of compositions between YFe_5 and YFe_4, a small change in composition will cause a large change in the amounts of microconstituents present. This makes it very difficult to obtain a pure one-phase structure in this region. The microstructure of iron-32.1 w/o yttrium is depicted in Figure 6f. This alloy is near the YFe_4 composition (28.4 w/o yttrium). The structure is nearly one phase, presumed to be YFe_4. A 35.6 w/o yttrium alloy was prepared to approximate the composition of YFe_3 (34.6 w/o yttrium) phase reported; however, the structure of the resultant alloy was two phase. No further information on this alloy was obtained; so the existence of YFe_3 was neither substantiated nor disproved.

The results of X-ray diffraction studies of iron-yttrium alloys are reported in Table 2. In analyzing these data, it was assumed that the X-ray method is relatively insensitive to small quantities of constitutent. Therefore, the use of metallography in conjunction with X-ray diffraction is necessary to obtain a complete understanding of the constitution of the samples being investigated.

TABLE 2. RESULTS OF X-RAY DIFFRACTION STUDIES OF IRON-YTTRIUM ALLOYS

Composition (Balance Iron), w/o	Heat Treatment	Intensities of Phase Patterns Observed			
		α-Iron	YFe_5	YFe_4	YFe_2
11 yttrium	As cast	S	VS	--	--
15.3 yttrium	As cast	VF	VS	--	--
20 yttrium	As cast	VVF	MS	--	--
24.2 yttrium	As cast	--	VS	VS	--
27 yttrium	As cast	--	MS	MS	--
32.1 yttrium	24 hr 800 C, water quenched	--		S	--
51.8 yttrium	1 week 800 C, furnace cooled	--	--	--	S

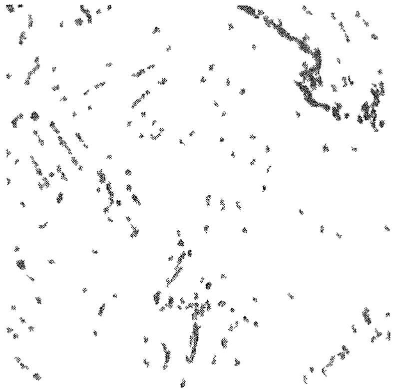
The structure of the YFe_5 phase is unknown. X-ray identification was effected by comparison with X-ray data available for the analogous $CeFe_5$ compound. The pattern corresponding to YFe_5 was detected in the iron alloys containing up to 27 w/o yttrium.



500X N57190

a. Iron-11 w/o Yttrium, As Cast

The white phase is YFe_5 and the light-gray particles are alpha iron.



250X RM10992

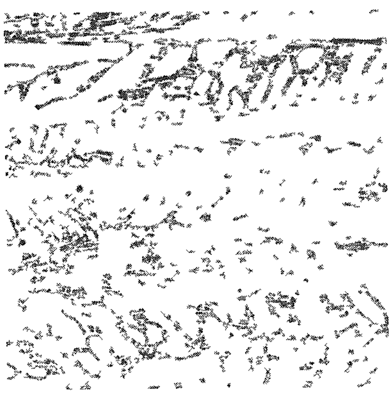
b. Iron-15.8 w/o Yttrium, (Oblique Lighting) As Cast

The herringbone-type pattern indicates that the iron-YFe_5 eutectic has been approximated.

250X RM11208

c. Iron-15.8 w/o Yttrium, Slowly Cooled From 1400 C

The alpha iron has agglomerated and spheroidized. Cracks in the YFe_5 matrix have not propagated through the more ductile alpha-iron particles.



250X N57186

d. Iron-20 w/o Yttrium, As Cast

The white matrix phase is YFe_5. It is surrounded by what is apparently a eutectic of alpha iron and YFe_5.

250X RM13657

e. Iron-24.2 w/o Yttrium, As Cast

YFe_5 and YFe_4 are present. The presence of YFe_4 indicates that the yttrium content exceeds that necessary to form YFe_5 (24.3 w/o yttrium), although the alloy is apparently 0.1 w/o yttrium short of the stoichiometric YFe_5 composition.

250X RM11919

f. Iron-32.1 w/o Yttrium, Held 24 Hr at 880 C, Water Quenched

This structure is nearly one phase, presumed to be YFe_4.

FIGURE 6. MICROSTRUCTURES EXHIBITED BY IRON-YTTRIUM ALLOYS

The iron-20 w/o yttrium alloy gave a very very faint diffraction pattern for alpha iron, substantiating the interpretation of its microstructure, Figure 6d. The X-ray pattern obtained from the iron-32.1 w/o yttrium alloy is typical of alloys containing only one phase. This pattern was taken to be that of YFe_4 (28.4 w/o yttrium), and was used as a standard to identify this phase in other alloys. One alloy containing 51.8 w/o yttrium was examined by X-ray methods and a phase isostructural to $MgCu_2$ was identified. This result was taken to indicate that the compound YFe_2 (44.2 w/o yttrium) exists.

The System Iron-Chromium-Yttrium

Study of the constitution of iron-20 to 40 w/o chromium alloys containing up to 6 w/o yttrium was carried out. In order to accurately define the phase relations in this region and gain an insight into the constitution of nearby areas, it was necessary to examine alloys whose compositions are outside of the area of interest. The results of this investigation are shown in Figures 3a through 3d. Phase relations were derived from thermal analyses, metallographic and X-ray diffraction examinations, and through consideration of the binary systems involved. Thermal-analysis data are presented in Table 3. Metallographic data are plotted in Figures 3a through 3d. X-ray diffraction data are shown in Table 4 and are plotted in Figures 3a through 3d.

The iron-20, -30, and -40 w/o chromium alloys, containing less than 6 w/o yttrium, usually show three thermal arrests. On heating, the first inflection in the curve or arrest occurs at 1320 to 1330 C, apparently indicating the melting of YFe_5. The second arrest occurs between 1467 and 1498 C and indicates the beginning of melting of the alpha iron-chromium phase. The final arrest occurs from 1429 to 1549 C and is associated with complete melting. In general, the addition of yttrium lowers the solidus and liquidus temperatures of the iron-chromium alloys. No evidence of melting at temperatures below 1320 C was observed in the iron-20 to 40 w/o chromium-yttrium alloys. Apparently melting associated with the binary iron-yttrium eutectic (1257 C) and any ternary eutectic resulting from the addition of chromium to the binary system is either too slight to be detected in these alloys or else melting associated with this eutectic is restricted to iron-rich alloys. On the basis of thermal analysis and metallographic data the latter appears more probable with YFe_5 existing in equilibrium with iron-20 to 40 w/o chromium alloys up to the melting point of this compound.

The phase relations existing at 1250 C (see Figure 3a) were derived mainly from metallographic examination of heat-treated alloys and X-ray diffraction examination of an iron-50 w/o chromium-3 w/o yttrium alloy, which indicates the existence of the alpha plus YFe_5 region. The microstructure of this alloy is shown in Figure 7. YFe_5 appears as light particles in an alpha matrix. The extent to which the alpha plus YFe_5 field extends toward the chromium corner is deduced from information obtained at lower temperatures. The other phase relations at 1250 C are inferred from the binary systems involved.

At 1100 C (Figure 3b) the phase relations are essentially the same as at 1250 C. The disappearance of liquid and the presence of YFe_3 and YFe_2 are inferred from the available information on the binary systems. Although alloy studies were not carried out in these regions, dashed lines are used to indicate the probable existence range of these compounds. The extent to which the alpha-plus-YFe_5 field is stable is not exactly established. X-ray diffraction studies of iron-50, -60, -65, and -70 w/o chromium

TABLE 3. THERMAL ANALYSES OF IRON-CHROMIUM-YTTRIUM ALLOYS

Composition (Balance Iron), w/o	Temperatures of Thermal Arrests, C		
20 Cr-0.04 Y[a]	--	1470	1495
20 Cr-0.10 Y	--	1484	1509
20 Cr-0.22 Y	--	1480	1497
20 Cr-0.29 Y	--	--	1503
20 Cr-0.5 Y[b]	--	--	1493
20 Cr-1 Y[b]	1327	--	1503
20 Cr-3 Y[b]	1335	--	1527
20 Cr-6 Y[b]	1329	--	1429
30 Cr-0.05 Y	--	1467	1495
30 Cr-0.10 Y	1328	1423	1505
30 Cr-0.15 Y	1322	1479	1505
30 Cr-0.18 Y	1318	1454	1505
30 Cr-0.25 Y	1324	1472	1509
30 Cr-0.73 Y	1321	1491	1508
30 Cr-2 Y[b]	1326	1471	1495
30 Cr-3 Y[b]	1321	1467	1481
30 Cr-6 Y[b]	1320	--	1479
40 Cr-0.25 Y	1321	--	1541
40 Cr-0.39 Y	1315	1498	1549
40 Cr-0.5 Y[b]	1319	1474	1540
40 Cr-1 Y[b]	1312	1470	1531
40 Cr-2 Y[b]	1316	1492	1539
40 Cr-5.2 Y	1303	1470	--
45 Cr-3 Y[b]	1309	1500	1552
50 Cr-3 Y[b]	1292	1495	1565
60 Cr-5 Y[b]	1253	--	1563
65 Cr-5 Y[b]	--	--	1561
70 Cr-5 Y[b]	--	1482	1551

(a) Arrests of the iron-20 w/o chromium-yttrium alloys were obtained by the inverse-rate method.

(b) Nominal composition.

TABLE 4. RESULTS OF X-RAY DIFFRACTION STUDIES OF IRON-CHROMIUM-YTTRIUM ALLOYS

Alloy Composition (Balance Iron), w/o	Heat Treatment[a]	Intensities of Phase Patterns Observed		
		Alpha Iron-Chromium	YFe_5	YFe_4
35 Cr-0.5 Y	10 days 900 C	VS	F	
35 Cr-3 Y	10 days 900 C	VS	VVF	
35 Cr-6 Y	10 days 900 C	VS	VF	
40 Cr-6 Y	10 days 900 C	VS	F	VVF
50 Cr-3 Y	3 hr 1250 C	VS	MF	
50 Cr-3 Y	4 hr 1100 C	VS	M	
60 Cr-5 Y	4 hr 1100 C	VS	MF	
65 Cr-5 Y	4 hr 1100 C	VS	F+	
70 Cr-5 Y	4 hr 1100 C	VS	F	

(a) Water quenched.

FIGURE 7. IRON-50 w/o CHROMIUM-3 w/o YTTRIUM ALLOY HELD 3 HR AT 1250 C AND WATER QUENCHED

YFe_5 appears as light particles in the alpha iron-chromium matrix.

alloys containing 3 to 5 w/o yttrium show that alpha iron plus YFe_5 are present; however, metallographic examination indicates that three phases are present in the 60, 65, and 70 w/o chromium alloys at 1100 C. Assuming that equilibrium was obtained, the third phase may be either YFe_4, some other yttrium-iron compound, or elemental yttrium.

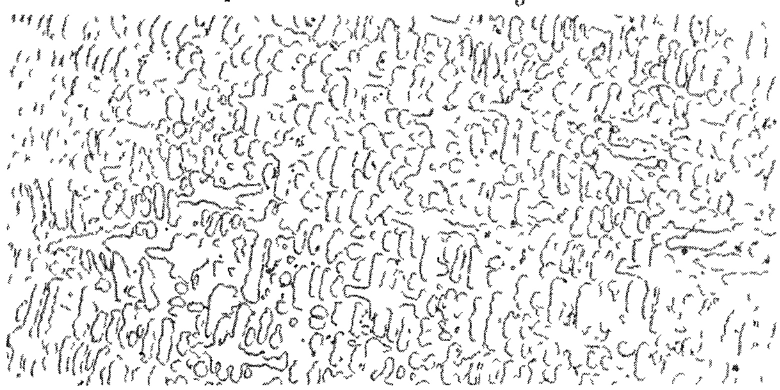
Phase equilibria at 900 C are presented in Figure 3c. Metallographic examinations show that the iron-35 w/o chromium-6 w/o yttrium and iron-40 w/o chromium-2.4 and 5.2 w/o yttrium alloys contain YFe_4 in addition to alpha and YFe_5. Inasmuch as only small quantities of YFe_4 are present, only a very very faint diffraction pattern of YFe_4 was obtained from the iron-40 w/o chromium-5.2 w/o yttrium alloy to substantiate the compound identification. Figure 8 shows this latter alloy; the small, light gray particles are YFe_4 in a matrix of alpha iron-chromium and YFe_5. A photomicrograph of iron-30 w/o chromium-5.2 w/o yttrium, quenched from 900 C is seen in Figure 9. The structure is alpha plus YFe_5 and is presented for comparison with the iron-40 w/o chromium-5.2 w/o yttrium alloy shown in Figure 8. The very small black inclusions are Y_2O_3. A microstructure typical of low-yttrium alloys in the alpha-plus-YFe_5 phase field is shown in Figure 10. This iron-35 w/o chromium-0.5 w/o yttrium alloy was quenched from 900 C.

Constitution at 600 C is altered by the appearance of sigma in the iron-chromium system as indicated in Figure 3d. Sigma-phase formation was established by hardness measurements and metallography. High hardness numbers, of the order of 1000 to 1200 VPH, were taken to indicate that sigma is present. Sigma formation is sluggish and a high degree of cold work is necessary to promote its formation in a reasonable length of time. Therefore, alloys that could not be cold worked (those containing more than 1 w/o yttrium) did not attain equilibrium and could not be used to ascertain constitution with regard to the presence of sigma. However, hardness studies on alloys containing 1 w/o yttrium or less established that YFe_5 is in equilibrium with sigma at 600 C. At this temperature, yttrium removes iron from the alpha iron-chromium solution to form YFe_5, leaving the matrix richer in chromium, and permitting the sigma composition to be attained, even in iron-rich alloys. Figure 11 shows the microstructure of an iron-40 w/o chromium alloy, cold reduced 80 per cent and heat treated at 600 C for 3 months. The white portion is alpha iron-chromium (hardness

250X RM12060

FIGURE 8. IRON-49 w/o CHROMIUM-5.2 w/o YTTRIUM ALLOY HELD 10 DAYS AT 900 C AND WATER QUENCHED

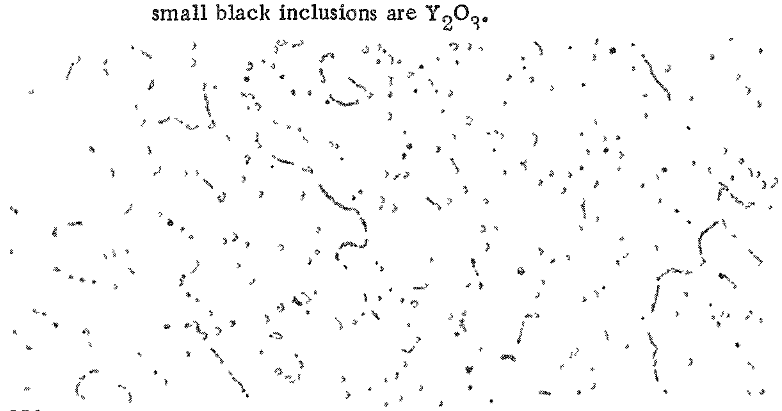
The small, light-gray particles are YFe_4 in a matrix of alpha iron-chromium and YFe_5.



250X RM12049

FIGURE 9. IRON-30 w/o CHROMIUM-6 w/o YTTRIUM ALLOY HELD 10 DAYS AT 900 C AND WATER QUENCHED

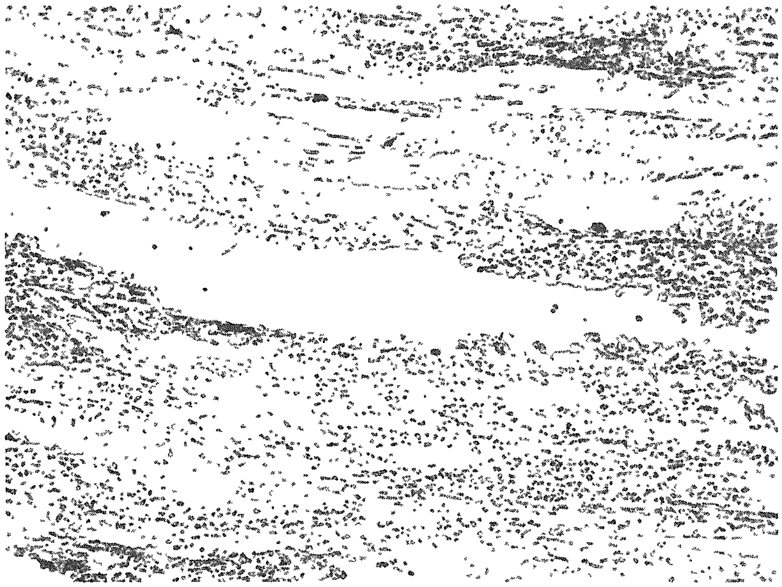
Structure is alpha iron-chromium plus YFe_5. The very small black inclusions are Y_2O_3.



250X RM12051

FIGURE 10. IRON-35 w/o CHROMIUM-0.5 w/o YTTRIUM ALLOY HELD 10 DAYS AT 900 C AND WATER QUENCHED

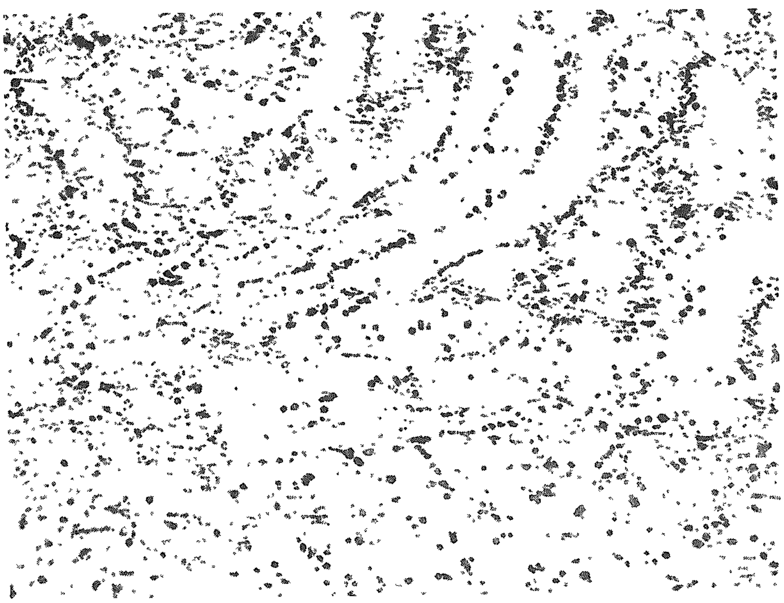
Microstructure is typical of low-yttrium alloys in the alpha-plus-YFe_5 phase field.



250X RM12475

FIGURE 11. IRON-40 w/o CHROMIUM ALLOY HELD 3 MONTHS AT 600 C AND WATER QUENCHED

The white portion is alpha iron-chromium (hardness 290 VPH) and the areas containing small particles are alpha plus sigma (hardness 600 VPH).



250X RM12478

FIGURE 12. IRON-40 w/o CHROMIUM-1 w/o YTTRIUM ALLOY HELD 3 MONTHS AT 600 C AND WATER QUENCHED

The black particles are holes representing the YFe_5, removed by the etching operation to bring out the structure of the sigma phase. The hardness of this sample is 600 VPH.

290 VPH) and the areas containing small particles are alpha plus sigma (hardness 600 VPH). A somewhat similar structure, Figure 12, is found in iron-40 w/o chromium-1 w/o yttrium, which was cold reduced and heat treated under the same conditions as the above iron-40 w/o chromium alloy. The black particles are holes representing the YFe_5, removed by the etching operation when etching to bring out the structure of the sigma phase. The hardness of this sample is 600 VPH, supporting the metallographic data and the interpretation that sigma formation took place.

SUMMARY AND CONCLUSIONS

The solid solubility of yttrium in iron-20, -30, and -40 w/o chromium was determined by metallographic methods and is indicated in Figure 1. Maximum solubility occurs near the solidus temperature, 1320 C, and is approximately 0.12 w/o yttrium. However, yttrium solubility decreases rapidly with decreasing temperature and at 600 C, the solubility is below 0.05 w/o yttrium. In general, it is apparent that yttrium solubility increases slightly with chromium content, all other factors being constant.

The constitution of the iron-rich alloys of the iron-yttrium system was investigated. Figure 2 shows the portion of the iron-yttrium phase diagram established by this study. The presence of YFe_5 was established, and a eutectic, existing between YFe_5 and iron, was found to occur at 1257 C. An intermetallic compound believed to be YFe_4 was found.

The phase relations existing in the iron-chromium-yttrium system were delineated for the region of 20-40 w/o chromium to 6 w/o yttrium. In addition, information obtained from alloys outside of the above area permitted establishment of tentative ternary relations for iron-chromium alloys containing small amounts of yttrium. These tentative phase relations are presented in Figure 3. Upon exceeding the solubility limit for yttrium in the iron-20, 30, and 40 w/o chromium alloys, YFe_5 appears. Above 815 C, the constitution of these alloys thus becomes alpha plus YFe_5. At 900 C, is as much as 6 w/o yttrium is present in iron-35 w/o chromium, and 2.4 w/o yttrium in iron-40 w/o chromium, the three-phase region, alpha plus YFe_5 plus YFe_4, is stable. Below 815 C, sigma phase is formed in the iron-chromium system and phase relations become altered. Sigma enters into equilibrium with YFe_5. The formation of YFe_5 effectively lowers the iron content of the alloy matrix, permitting the attainment of the sigma-phase composition; therefore, sigma can exist even in very iron-rich alloys as shown in Figure 3d.

REFERENCES

(1) Epstein, S. G., Bauer, A. A., and Dickerson, R. F., "Solubility Limits of Yttrium and the Lanthanide Rare-Earth Elements in Chromium-Iron Alloys", BMI-1376 (September 1, 1959).

(2) Domagala, R. F., "Phase Diagram Studies", Progress Report No. 3 APEX-450 (July 1 - September 30, 1958). Secret.

MSF:AAB/slr/mrm