THE TERNARY SYSTEM

IRON-CHROMIUM-MOLYBDENUM

AT 1200°F

Theeis by

Spencer Roe Baen

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ABSTRACT

The phase boundaries of the irou-chronium-molybdenum termary system have been investigated at 1200° F. One-hundred and eighty alloys were prepared by the method of powder metallurgy for this study. The alloys were aged in vacuum (10^{-4} mm Hg or better) for ten days at 1200° F. Following the aging treatment the alloys were rapidly cooled to room temperature. The primary research tools were the methods of X-ray diffraction and microscopy as applied to the determination of phase boundaries in alloy systems. Microhardness tests were used in conjunction with microscopy for the identification of phases for some alloys. The results of the present investigation in the three binary systems are compared with the rosults of previous investigators. It was found that the sigma phase of the Fe-Cr binary system is stabilized by the addition of molybdenum and that this brittle phase is present over a large range of compositions.

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I. INTRODUCTION

The determination of the phase boundaries of basic alloy systems is a fundamental prelude to many advancements in theoretical metallurgy. Certain developments such as Hume-Rothery's theory of the formation of electron compounds were to a large extent stimulated by accurate work on equilibrium diagrams.

Phase diagrams of alloy systems are also valuable as a guide to the systematic development of commercial alloys. Without phase diagrams the development of useful alloys is, for the most part, empirical and is usually quite costly.

The purpose of this research is to determine accurately the phase boundaries of the ternary system iron-chromium-molybdenum at 1200° F. It was not feasible to investigate the constitution of this system as a function of temperature because of the time element. The 1200° F temperature level was selected because of the belief that equilibrium at this temperature could be attained in a reasonable length of time and, also, because the loss of chromium by evaporation is quite small at this temperature.

The phase boundaries of this ternary system were determined by X-ray diffraction and microscopy techniques. Microhardness tests were used in conjunction with microscopy as an aid in the identification of the various phases in some alloys. These methods are discussed below.

The method of X-ray diffraction for the determination of phase boundaries in ternary systems is well described in textbooks (for

example, Barrett (1)*) and has been successfully applied to the solution of numerous ternary systems (for example, (2), (3), and (4)). Briefly, the method is as follows:

The variation of the lattice spacings as a function of composition in the one-phase regions of the ternary system is determined from diffraction patterns of alloys in these regions. This is the first step in the application of the X-ray method.

Alloys in a three-phase region consist of three phases whose compositions correspond to the alloys at the apices of the threephase triangle. The lattice spacings of the three phases are then determined from diffraction patterns of alloys in the three-phase region. Comparison of these spacings with the spacings in the onsphase regions which touch the corners of the three-phase triangle establishes the positions of the corners, hence the whole triangular region. By locating the three-phase triangles in this manner, one boundary is determined for each of the adjacent two-phase regions.

The remaining boundaries of each two-phase region are determined by the following principle. The composition of each phase in an alloy consisting of two phases is the same as the composition at the corresponding end of the tie line which passes through the alloy on the ternary diagram. Comparison of the lattice spacings of the phases in a series of alloys will then establish points on the boundary of

Note: For an excellent reference on the basic principles of phase diagrams, see either (5) or (6). * Numbers in parentheses refer to references at the end of this thesis.

the region. The ternary diagram is completely determined when all of the phase boundaries of the three-phase and two-phase regions have been located.

The approximate locations of the phase boundaries can be estimated from a few carefully chosen alloys. Additional alloys are then prepared with the object of defining the phase boundaries more exactly.

Microscopy is used to determine phase boundaries by visual investigations of the microstructure of alloys. The various phases are identified by the use of etchants which act selectively. A singlephase alloy will show a uniform structure which is characteristic of the particular phase. When a phase boundary has been crossed and an alloy in a two-phase region is observed microscopically, the presence of the second phase can usually be detected. The structure of a three-phase alloy will reveal the presence of the three phases, each distributed in some characteristic manner.

Each of the above methods is subject to certain limitations and each has relative merits which supplement the other's shortcomings.

X-ray diffraction methods, for example, are limited to cases where a transformation of a phase does not occur during the quenching operation. Microscopy, on the other hand, is capable of determining phase boundaries at the temperature from which the specimens are quenched even if decomposition of one phase occurs during quenching.

Microscopy is dependent upon the existence of suitable etchants which will identify the various phases. There are instances where

this method fails for the lack of a suitable stehing reagent. Microscopic observations are difficult to interpret when the grain size of a sample is too small or when a precipitate is too finely divided. X-ray diffraction, however, will, in the majority of cases, determine the phases of the alloy regardless of the distribution of the phases or etching obtracteristics.

Provided suitable etchants can be found, the presence of a second phase in small amounts can usually be detected microscopically. The detection of a second phase in small amounts by X-ray diffraction depends to a great extent upon the alloy phases and the radiation employed. With microscopy, one can readily detect a second phase which would not be detected by X-ray analysis. The detection of a second phase in small amounts is not, however, a requirement for the fixing of phase boundaries by the X-ray method.

The accuracy of a phase boundary determined by X-ray diffraction methods depends on the angle at which the tie lines intersect the lattice parameter contours in the singlo-phase regions. Where the lines are nearly parallel, the accuracy is poor and the phase boundaries should be determined by microscopy.

Recently, the subject of X-ray diffraction versus microscopy has received considerable attention. Hume-Rothery and Raynor (7) critically discuss the X-ray diffraction technique and come to the conclusion that this method should be used in conjunction with microscopy. However, other authors (Owen and Morris (8)) believe that the phase boundaries determined by X-ray methods alone are more

likely to represent the system than those determined by microscopy. The attraction for the *k*-ray method is mainly its expediency. Relatively few alloys are necessary to establish the important features of the phase boundaries. This method is especially attractive in the study of ternary systems, where, if composition intervals of 2.5 per cent were used, 861 alloys would be required to cover the system.

In view of the preceding discussion, X-ray diffraction and microscopy should be used in conjunction for an investigation of this nature. The necessity for their complementary use is well demonstrated in this investigation of the phase boundaries of the Pe-Cr-Mo system.

The iron-chromium-molybdenum ternary system was chosen for this research project for several reasons. First, the constitution of this system has not been thoroughly investigated. Second, there is current interest in alloys of this system for heat, resistant gas turbine alloys. Third, an equilibrium phase of this system is the "Sigma Phase" which is now the subject of intensive study because of its brittle nature and its adverse effect on many alloys. The beneficial effect of the "Sigma Phase" as a precipitation hardening agent in other alloys is also the subject of recent researches.

A. Previous Work on the Ternary Fe-Cr-Mo System

A survey of the literature reveals that there is no published work on the phase boundaries of this ternary system at any temperature lovel. The previous work that has been done is limited to the investigation of chromium-base Fe-Cr-Mo alloys for use in gas turbines.

During the war and for a short period thereafter, the motivation of the metallurgist working on the development of alloys for use in gas turbines was to produce the best possible alloy in the shortest possible time. High temperature alloys used during the war and currently for gas turbine blading have an operating limit of approximately 1500° F. These alloys are known as "super alloys" and consist of the nickel-base Hastelloys, the cobalt-base alloy "Vitallium", the Co-Cr-Ni alloy N-155, and others. The development of heat resistant alloys with superior strength at or above 1600° F for use as gas turbine blades rotating in an oxidizing atmosphere remains a goal for the metallurgist.

Research on prospective gas turbine alloys by Parke and Bens (9) has shown that the most promising alloys possessing superior properties at 1600° F are chromium-base alloys of the system iron-chromiummolybdenum. Stress-rupture tests by these investigators have shown alloys of the composition range 60 Cr, 15-25 Fe, 25-15 Mo (per cent by weight) are capable of supporting 20,000 lbs/sq in. for as long as 1042 hours and are capable of supporting 37,500 lbs/sq in. for as long as 65 hours at 1600° F. The above strengths represent the best values obtained. A wide variation in strength was observed, and was attributed to the lack of control of grain size.

It is also interesting to note that Parke and Bens, in the discussion following their paper, state that the "Sigma Phase" was found as a constituent of these alloys.

More recent research on chromium-base alloys by Havekotte (10)

has shown that an alloy of the composition 58 Cr, 15 Fe, 25 Mo, 2 Ti (per cent by weight) was capable of supporting a stress of 40,000 lbs/sq in. at 1600° F for more than 500 hours. Heattreated alloys of the same composition were reported to withstand the same stress level and temperature for 1764 hours.

These investigations, although concerned primarily with overcoming fabrication difficulties, have demonstrated the superior high temperature properties of chromium-base alloys. During the war, the development of these alloys was so important that the basic research on the ternary system was not undertaken. The phase boundaries of the Fe-Cr-Me system as a function of composition and temperature must be known before these gas turbine alloys can be developed systematically. Such knowledge would indicate which alloys would be susceptible to the benefit of the precipitation hardening effect of the "Sigma Phase".

B. The Sigma Phase

The sigma phase, according to Bain and Griffiths (11), is "A clear-etching, corundum-hard, brittle, non-magnetic constituent, usually filled with faint cracks". It was first discovered by the above investigators in a study of the Fe-Cr-Ni system in 1927, and was also found to exist in the Fe-Cr binary system. Since its discovery in the Fe-Cr system, its analogue has been found in five other binary systems. For example, the sigma structure was discovered in the Fe-V system by devor and Jellinghouse (12) in 1930; the gamma

phase in the Cr-Co system was shown to be isomorphous with sigma by Elsea and colleagues (13) in 1948; and more recently Goldschmidt (14) in 1945 showed that the structure of the high temperature zeta phase in the Fe-Mo system is that of sigma. It has been suggested by Beck and Manly (15) that the sigma structure might exist in the systems V-Co and V-Ni. Duwez and the author (16) have shown that the sigma phase does exist in these two systems.

Relatively little is known concerning the sigma phase and much of that which is known has been determined only on an empirical basis. The crystal structure of this phase has not been determined and the mechanism of its formation has not been investigated thoroughly. The reaction leading to the formation of sigma from the solid solution state is considered by many investigators to be sluggish. There is, however, no quantitative data on transformation rates. Many investigators state that small amounts of strain seem to accelerate the formation of sigma.

The influence of the sigma phase on the physical properties of heat resistant stainless steels has been studied by a large number of investigators. It is known that the presence of sigma in many of these alloys seriously affects impact and corrosion resistance. Failures of heat resisting stainless steels in service have been few but increasing knowledge of potential troubles has stimulated research on the effect and equilibrium range of the sigma phase in alloy systems. A comprehensive survey of the practical importance of the sigma phase may be found in a publication by Foley (17).

C. Previous Work on the Fe-Cr, Fe-Ho, and Cr-Mo Binary Systems

Since the Fe-Cr-Mo alloys are closely related to the binary systems Fe-Cr, Fe-Mo, and Cr-Mo, it is important to review the re-

The Iron-Chromium System

The iron-chromium system has received considerable attention in the past years because of its relationship to the stainless steels. E. G. Bain (18) in 1926 believed that the binary system consisted of an uninterrupted series of solid solutions except for the gamma loop. In 1927, Bain and Griffiths announced the presence of the sigma phase in this system (see above). For a few years following the announcement of this brittle constituent, the sigma phase in this system was a controversial subject. Adcoch (19) in 1931 denied its existence; Preston (20) in 1932 published an X-ray diffraction study of the binary which showed no sigma phase. Preston's data on the variation of lattice parameter as a function of composition, however, clearly indicated an abnormal behavior of these alloys. As late as 1937, literature (Jenkins (21)) was appearing in which the sigma phase was not shown to be a part of the iron-chromium system.

Of the more recent work on the signa phase in the Fe-Cr binary system, by far the most complete and accurate work was done by Cook and Jones (22) in 1943. These investigators used microscopy in conjunction with X-ray diffraction to establish the phase boundaries

involving the sigma phase shown in Fig. 1. These boundaries conform essentially with the earlier work of Wever and Jellinghouse (23), but show wider limits for the alpha plus sigma regions.

The Fe-Cr binary system shown in Fig. 1 incorporates the results of Cook and Jones with the diagram presented in the Metals Handbook (24).

The Iron-Molybdenum System

The iron-molybdenum binary system, as shown in Fig. 2 (24), is a compromise between the work of Sykes (25) and Takei and Murakami (26). Sykes employed microscopy alone, whereas Takei and Murakami used microscopy, dilatometry, magnetic measurements, and thermal analysis. These investigators agreed as to the phase boundaries at 1200° F but disagreed in the more complicated regions of liquid plus epsilon (8) and liquid plus zeta (ζ).

The epsilon phase is given by a very narrow range and is designated by the above authors as the compound FegMe_2 . Arnfelt and Westgren (27) have designated the structure of the epsilon phase as rhombohedral of the space group D_{3d}^5 with parameters a ≈ 8.97 Å and $\propto = 30^{\circ}38.6^{\circ}$. This structure requires thirteen atoms and the compound is designated Fe7Mo6 by these authors. However, the composition corresponding to Fe7Mo6 is not included in the one-phase epsilon region of Fig. 2. This apparent conflict will be discussed later.

As stated proviously, the structure of the zeta phase was found by Goldschmidt (14) to be isomorphous with the sigma phase of the

iron-chromium system.

The Chromium-Molybdenum System

The chromium-molybdenum system shown in Fig. 3 (24) indicates that chromium and molybdenum are completely coluble in all proportions in the solid state. Rubaschewski and Schneider (20) and Trzebiatowsky and colleagues (29) concur in this result. Trzebiatowsky and colleagues present X-ray diffraction data on the variation of the lattice parameter of these alloys as a function of composition.



The Iron-Chromium Binary System. (After Cook and Jones and Metals Handbook) Fig. I :



Binary System (Metals Handbook). Iron - Molybdenum The Fig. 2 :



II. EXPERIMENTAL PROCEDURE

A. Preparation of Alloys

The alloys studied in this investigation were prepared by powder metallurgy. Alloys of high purity may be prepared from pure metal powders by this method. The desired proportions of the metal powders are thoroughly mixed, compacted, and alloyed by diffusion in the solid state (sintering) in furnaces with controlled atmospheres. The complexities of the solidification process which produce inhomogeneities in alloys prepared by melting and the attending difficulties of contamination at the high temperature required for melting are avoided. Usually it is not necessary to determine the composition of alloys prepared by this method. Where volatile constituents are used, it is necessary to investigate the accuracy of the composition of the alloys.

The analysis in weight per cent and the source of the component metal powders used for the preparation of alloys are tabulated below:

TABLE I

Analysis of Component Metal Powders

| Metal | Source | | Analysis |
|------------|--|---|---|
| Iron | Carbonyl iron, type L Charles Hardy, Inc. | 0.008% C 0.05 % Si 0.05 % Mn 0.05 % Ca | Traces of Ni, Cu, Mo, Ti, and Cr. |
| Chromium | Electrolytic Grade Charles Hardy, Inc. | 0.1% Na 0.05% Ca | Traces of Cu, Al, Mg, Si, Co, and Mn. |
| Molybdenum | Reduced from Molybdic Acid | 0.25 % Fe 0.1 % Ni 0.05 % Ca 0.05 % Cr | Traces of Ti, Ba, Co, and Sr. |

Molybdenum powder of sufficient purity was not available commercially and was prepared at the Jet Propulsion Laboratory especially for this investigation. Chemically pure molybdic acid (MoO $_{5}H_{2}O$) was decomposed by heating at about 1200° F to obtain MoO₃. This exide was then reduced in dry, pure hydrogen for four hours at 2300° F. The molybdenum powder was then screened and the fraction which passed through a 200-mesh screen was utilized for the preparation of alloys.

The chromium powder was minus 500-mesh and the iron powder was minus 525-mesh. The particle sizes of the molybdenum, chromium, and iron powders, corresponding to the above screen sizes, were less than 74, 46, and 43 microns in diameter, respectively.

Alloy composition was based on atomic percentages. This choice was made for the following reason. Lattice parameters of substitutional solid solutions are functions of the atomic diameters of the components. Therefore, atomic percentages are more significant than weight percentages.

Alloys were prepared from the three metal powders by weighing out the desired smount of the individual components on an analytical balance. The alloys were usually made up in 10 gram lots. In cases where a small percentage of one metal was desired, the samples were made up in 20 gram lots. This was done to increase the accuracy of the composition of the mixture. The individual components were weighed to within an accuracy of ± 0.0005 grams.

Subsequent to weighing, the powders were sealed in a glass jar. The glass jars were placed in a small mixing mill and the powders were

mixed for periods of 48 hours or longer.

The mixed metal powders were then cospected in 5 gran lots in a cylindrical, hardened metal die approximately 1/2 inch in diameter, under a pressure of 80,000 lbs/sq in. The compacted specimens were cylinders 1/2 inch in diameter and approximately 1/4 inch thick. These compacts were then sintered in a tubular Globar furnace for four hours at 2500° F in a continuously flowing atmosphere of pure, dry hydrogen. An open tray of pure chromium powder was placed upstream of the compacts in the flow of hydrogen as a "getter" to increase the purity of the hydrogen.

The alloys were furnace cooled from the clutering temperature and the shrinkage or expansion of the compact during sintering was dotermined. Since the alloys were to be examined by microscopy, it was desirous that they be as dense as possible? If the alloy had expanded, it was crushed in a tool steel mortar, passed through an 80mesh screen, re-pressed and resintered as described above. The thermal history of the various alloys is included in Table II.

After sintering, the compacts were out on a diameter along the axis of the cylinder and placed in evacuated (at least 10^{-4} nm Hg) silica tubes. The alloys were then aged for ten days at 1200° F. Following the aging treatment the silica tubes containing the alloys were rapidly cooled to room temperature by quenching in water. The heat transfer was sufficient to cool the alloys to approximately room temperature in loss than two minutes.

The temperature of the furnace in which the alloys were aged was

controlled by use of a "Wheelco" controller. The temperature was maintained at $1200 \pm 20^{\circ}$ F.

One-hundred and eighty alloys were made for the study of the phase boundaries of this system. The composition of these alloys is tabulated in Table II and is shown graphically in Fig. 7. The alloys are numbered 1 through 185; however, alloys number 160, 161 and 165 were not made.

B. 1-ray Diffraction Technique

A Picker X-ray Diffraction Unit utilizing powder cameras of two diameters was used to obtain the X-ray diffraction data for this investigation. The large camera was 214.86 mm in diameter and the small camera was 71.62 mm in diameter. These cameras will henceforth be designated "large" and "small" camera, respectively.

Three characteristic radiations were used. The following X_{α_1} wave lengths in Angstrom units were used for computational purposes:

Copper - Cu $K_{\alpha]}$ - 1.54050 Å Cobalt - Co $X_{\alpha]}$ - 1.78890 Å Chromium - Cr $K_{\alpha]}$ - 2.28962 Å

A nickel filter and a vanadium oxide filter were used for filtering of the Cu K_{β} and the Cr K_{β} wave lengths, respectively. The iron in the specimens served for filtering of the Co K_{β} radiation. Co K_{α_1} radiation was used for the majority of the alloys in spite of the fact that for alloys with large amounts of chromium the general background darkening of the films was objectionable. This radiation was used primarily in order to follow the variation with composition in the spacings of a persistent, easily identified set of lines in the diffraction pattern of the signa phase.

Powder samples of the alloys for X-ray diffraction analysis were obtained by two methods:

1. If the alloy was ductile, powders were produced by filing. The surface metal was filed away to a depth on the order of 1/16 inch before sample filings were collected. In this manner any surface depletion of a constituent or surface contamination effects were avoided. Powder samples were also produced by filing from alleys that were porcus and brittle. A clean pattern maker's file was used for filing. In all cases, the sample was taken from below the surface.

2. In cases where the alloy was hard and difficult to file, the powders were obtained by crushing a portion of the alloy in a tool steel mortar. The alloy was crushed until all of the particles would pass through an 80-mesh screen. This was done to obtain a representative sample. The majority of the alloys of this system possessed so little ductility that they were empable of being crushed and screened through an 80-mesh screen with no difficulty.

Powder samples obtained as described above were coated on amorphous silice fibres (0.10 to 0.15 mm diameter). Mineral oil was used as an adhesive.

The specimens were centered in the large camera by observing the shadow of the specimen on a flourescent screen and making adjustments until the shadow remained stationary as the specimen was rotated. The

specimens were centered in the small camera prior to loading the film. The specimen was first centered on its specimen stage by use of an external chuck. The centering was checked prior to the insertion of the film by rotating the specimen in the camera chuck. Adjustments were made if required. Contering was finally checked by observing the shadow of the specimen in the X-ray beam with the camera loaded and the specimen rotating.

The large camera was calibrated by comparing computed interplanar spacings of calcite with those observed from a diffraction pattern of this material. Two conveniently located knife edges in the camera, which cast sharp shadows on the film, were found to be located so as to include 340 degrees of arc of exposed film. These references on the film were used as standard; their use automatically corrected for film shrinkage.

The arrangement of the film used in the large camera is illustrated in Fig. 4. The distances measured for computation of the Bragg angles for the various reflecting atomic planes are also illustrated in Fig. 4.



Fig. 4 - Arrangement of film used in large camera.

The values of twice the Bragg angle, 20, for diffraction records using this camera were converted to interplanar spacings, 'd, by use of a table of interplanar spacings in Angetron units versus 20.

The film in the small camera was mounted following the Straumanis technique (Illustrated in Fig. 5.) for which it is possible to eliminate film shrinkage errors directly.



Fig. 5 - Arrangement of film used in small camera.

Film used in this manner has diffraction lines for Bragg angles less than 45 degrees symmetrically spaced about $\Theta = 0$ degrees and lines for Θ greater than 45 degrees symmetrically spaced about $\Theta = 90$ degrees. Therefore, the location of $\Theta = 0$ degrees and $\Theta = 90$ degrees is defined and the distance on the film corresponding to the arc subtended by Bragg angles 0 to 90 degrees may be determined. This distance, X₀, varies from film to film due to shrinkage in processing of the film. Computing the Bragg angle for the various diffraction lines by $\Theta = 90X/X_0^2$ corrects for film shrinkage. This necessarily assumes the film shrinkage to be uniform along the length of the film. Unterplanar spacings, d, are then computed from the Bragg law $n\lambda = 2$ d Sin Θ .

The computation of interplanar spacings from films obtained with the small camera was essentially as described above. A table of interplanar spacings, d, as a function of distance, x, measured on a film of standard length was available. To facilitate the compatation of interplanar spacings, the observed values for x were corrected for film shrinkage by applying a proportional correction to the measured x. This method was checked using pure annealed iron, chromium, and molybdenum powders, the parameters of which had been previously determined by the use of the large camera.

The X-ray diffraction films were read using a visual film reader. The position of a diffraction line was measured to within ± 0.1 mm.

The small camera was used extensively in this investigation because the accuracy of the lattice spacings so determined was considered sufficient. Where greater accuracy was desired in critical alloys, the large camera was used. Alloys that were analysed by use of the large camera were annealed (2 to 6 hrs.) in the powder form in vacuum at 1200° F to remove any cold work that might be present. Internal stresses in powder samples produce broad diffraction lines, particularly in patterns obtained with cameras of large diameter.

The errors involved in the use of powder cameras for the

determination of interplanar spacings and lattice parameters are investigated in Appendix II. The method used in determining corrected lattice parameters of the body-centered-cubic phases is also illustrated in this appendix.

The lattice parameters of the body-centered-cubic phase which occurred in the alloys after 10 days at 1200° F are tabulated in Appendix I (Table II). The parameters computed from data obtained using the small camera are accurate to within ± 0.002 Å and the parameters computed using data obtained with the large camera are accurate to within ± 0.0007 Å.

C. Metallographic and Microhardness Technique

The majority of the alloys were prepared for metallographic observation by mechanical polishing and electrolytic etching.

The electrolytes used for the electrolytic etching were primarily (1) 10 per cent oxalic acid and (2) perchloric acid solution. The perchloric acid solution is the standard electrolyte recommended by the Adolph Buehler Co. for ferrous alloys. The etchants used for producing the structures shown in the photomicrographs in this thesis are indicated beneath the photomicrographs.

The etching of a porous alloy is sensitive to the time of etching since the etchant enlarges the voids, leaving a very undesirable surface for metallographic observation. Many of the alloys were porous. A number of the alloys were too porous to be of use for metallographic examination.

An attempt was made to find an etchant which would positively identify the sigma phase. Alloy No. 120 (52Fe - 48 Cr) in the Fe-Cr binary system was used for the investigation of a number of etchants suggested in the literature by various authors. This alloy when quenched from 2300° F consists of one phase (solid solution). Aging for 10 days at 1200° F completely transforms the alloy to sigma. Two samples of this alloy, one in the solid solution state and one in the transformed sigma state, were used in this study.

The etchants investigated were:

- 1. Modified Murakami Reagent used at boiling temperature
- 2. Marble's Reagent
- 3. Vilella's Reagent used electrolytically
- 4. Aqua Regia
- 5. 50 per cent aqueous solutions of Hydrochloric Acid
- 6. 10 per cent aqueous solution of sodium cyanide used electrolytically
- 7. 10 per cent exalic acid used electrolytically
- 8. Perchloric acid solution used electrolytically

The structures observed in etched surfaces of this alloy were alike regardless of the phase present or of the etchant used. (See Fig. 17c (solid solution) and Fig. 17d (sigma).) Hence, it was not possible to rely on etchants alone to distinguish the sigma phase.

Microhardness tests were used for the identification of phases in etched surfaces of some alloys. For this work a "Tukon Superficial Hardness Tester" with a "Knoop" type diamond pyramid indentor was used. The "Knoop" pyramid has a longitudinal angle of 172 degrees 30 minutes and a transverse angle of 130 degrees. The impression is rhombic in shape with a ratio of long diagonal to short diagonal of 7.11 to 1. This tester is manufactured by Wilson Mechanical Instrument Co. Phases were identified primarily by a "scratch test" using the diamond pyramid with a 25 gram load to produce a controlled scratch across the various phases in the alloy. By observing the width of the scratch, the relative hardness of these phases was determined.

The hardness of the alloys was determined using a 300 gram load. With this load, the impression of the pyramid was not as sensitive to minute differences within the grains as with lower loads. The length of the long diagonal of the impression was determined with a microscope equipped with a filar micrometer eyepiece. A magnification of lOOX was used. This length was then converted to Knoop Hardness numbers by use of a calibration chart supplied by the manufacturer. The hardness, in Knoop hardness numbers, of the alloys is recorded in Table II. These hardness values are the average of at least three measured values.

III. THE Fo-Cr-Mo TERNARY SYSTEM

The experimental results and specimen compositions are presented in this section because of the belief that the reader should have this information available during the development of the phase boundaries.

The ternary phase diagram at 1200° F, as determined by this investigation, is presented in Fig. 6. The contours of equal lattice parameter in the alpha (\propto) solid solution region and in the ironrich alpha prime (\propto ') solid solution region of this figure are labeled in Angstrom units. The variation with composition of the cell parameters of the sigma phase in the sigma region is indicated in terms of the parameter "a". The parameter "a" is the length of the cell base of a tentative tetragonal structure which is developed in Appendix III.

The alloy compositions used in this study are shown in Fig. 7. Fig. 7 also shows the number of phases present in these alloys at 1200° F.

Examples of typical X-ray diffraction patterns are shown in Fig. 6. These patterns were obtained with cobalt radiation and the 71.86 mm camera. The films were enlarged slightly (1.03X) when reproduced.

The phase boundaries of the ternary system shown in Fig. 6 are developed in the following sections.





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IV. THE PHASE BOUNDARIES OF THE ALPHA PLUS SIGMA ($\propto + \sigma$) REGION

The phase boundaries of the alpha plus signa region were determined primarily by the X-ray method.

Bafore proceeding with the development of the phase boundaries of this region, the principles involved in such a determination will be demonstrated. Consider the portion of an isothermal section of the ternary system shown below.



The lines in the beta region are contour lines which indicate compositions having equal lattice parameters. The lines in the gamma region are also contour lines and indicate compositions that have equal parameters of this phase. Contours in these regions are not necessarily straight lines. However, in some cases, they may be approximated by straight lines.

In the $\beta + \gamma$ region, the lines are straight and are called

"tie lines". Alloys which lie on the same tie line are composed of two phases whose compositions are determined by the end points of the tie line. For example, an alloy of composition b is located on the tie line abc. This alloy consists of two phases whose compositions are given by the compositions a and c. The relative proportions of the beta phase and the gamma phase in this alloy are given by bc/ac and ab/ac, respectively.

All alloys whose compositions lie on the tie line abc, contain phases whose parameters are given by the parameters of the contours labeled (1) in the beta region and (2) in the gamma region. Therefore, the parameter contours in a two-phase region are equivalent to tie lines and are straight lines. The intersection of parameter contours in the two-phase region with parameter contours in the onephase regions determines points on the phase boundaries.

If the parameter contours of the beta phase alone are plotted on the composition triangle, points on the boundary between this region and the two-phase region are located at the discontinuities in the parameter contours. Points on the boundary between the $\beta + \gamma$ region and the γ region are located by considering the parameter contours of the γ phase.

The accuracy of the location of a phase boundary determined by this method depends on the angle of intersection of the parameter contours. If the straight line contours in the two-phase region intersect contours in the one-phase region at an obtuse angle, the accuracy of the location of the boundary is poor.

To establish parameter contours, curves of lattice parameter versus composition are first established for the binary systems and then for sections catting across the various phase regions. Compositions corresponding to previously determined lattice parameter values are then taken from these curves and are crossplotted on the composition triangle. Contours are then drawn through points of equal lattice parameter.

The phase boundaries of the $\prec + \sigma$ region in the Fe-Gr-Mo system were determined by the method discussed above.

It is most convenient to determine the phase boundary between the \propto and the $\propto +\sigma$ regions first.

The variation of the lattice parameter of the body-conteredcubic alpha phase as a function of composition was first established for the adjoining binary systems. The variation of the lattice parameter with composition was then established for section lines cutting across the ternary solid solution region and the two-phase $\prec + \sigma$ region. These sections were chosen such that the percentage of one of the component metals remained constant or the ratio of the percentages of two of the component metals remained constant.

The variation of lattice parameter as a function of composition in the Cr-Mo binary system as determined in this investigation is compared for convenience with the results of Trzebiatowsky and colleagues (28) in Fig. 9. In Fig. 10 the results of Preston (20) regarding the variation of lattice parameter in the Fe-Cr binary system are compared with the results of this study.

The variation of lattice parameter as a function of molybdenum content along a section of constant 10 per cent iron is shown in Fig. 11. Figs. 12 and 13 show the variation of lattice parameter with molybdenum content for sections of constant chromium content (60 and 70 per cent respectively). Values of composition corresponding to lattice parameter increments of 0.01 Å were interpolated from these curves. These values are plotted in Fig. 14. The data for the sections which were investigated are shown in Fig. 14. An attempt was made to utilize sections which would intersect contours as close to right angles as practical. In this manner, the error in the composition corresponding to a particular lattice parameter was minimized.

Parameter contours were drawn through points of equal lattice parameter as shown in Fig. 14. The intersection of the straight line contours in the $\prec + \sigma$ region with their corresponding contours in the alpha solid solution region determined points on the boundary between these two regions. In the determination of the points on this boundary, contours for increments of 0.01 Å were used. In Fig. 14 contours are shown only for values of lattice parameter in increments of 0.02 Å; however, points for values of lattice parameter in increments of 0.01 Å are included. For concentrations of melybdenum less than approximately 25 per cent, the parameter contours in the $\prec + \sigma$ region intersect contours in the \prec region at an obtuse angle. Therefore, the location of the phase boundary in this region is uncertain and the boundary is shown as a dashed line

in Fig. 6.

To obtain the boundary between the σ and the $\prec + \sigma$ regions, the variation of interplanar spacings with composition of the sigma phase was first established in the one-phase sigma region. Points on the boundary between these two regions were then located by constructing the tie line through each of the alloys in the twophase region. The slopes of these tie lines were determined on the basis of the lattice parameter contours of the alpha phase in this region. The end point of the tie line which passed through a particular alloy was located by comparing the interplanar spacings of the sigma phase in the alloy with the contours in the one-phase sigma region.

The interplanar spacings used to determine contours in the sigma region were the spacings, d, of a persistent, easily identified set of lines in the back reflection range (i.e. Bragg angle $\Theta > 60^{\circ}$ for cobalt radiation) of the diffraction pattern of this phase. These spacings correspond to the lines labeled 1 and 2 in Figs. 15 and 16. In particular, the interplanar spacing of the line designated 1 in these figures was used to determine interplanar spacing contours for the sigma region. The spacing of this reflection varied from approximately 0.900 Å to approximately 1.030 Å, and the maximum error in its determination was approximately 0.002 Å (Appendix II).

Three section lines through the one-phase signa region were used to determine interplanar spacing contours in this region.

Fig. 15 shows the variation of interplanar spacings for eight reflections as a function of molybdenum content along the line from the center of the Fe-Cr binary system to the molybdenum corner (i.e. variation of molybdenum in equal proportions of iron and chromium). The variation in the spacings of the same eight reflections as a function of molybdenum content along the section of constant 50 per cent iron is shown in Fig. 16. As can be seen from these figures, the interplanar spacings along these lines are a linear function of molybdenum content within the limits of experimental accuracy. In addition to the above sections, the variation of interplanar spacings as a function of per cent molybdenum along the line through alloys No. 102, 78, 99, and 74 (See Fig. 7.) was determined. The variation in the spacing of the reflection designated 1 in Figs. 15 and 16 was used to determine interplanar spacing contours in the one-phase signa region for the sections which were discussed above.

The phase boundary between the σ and the $\alpha + \sigma$ regions was then established using these contours and the tie lines which were drawn through experimental points. The above interplanar spacing of the sigma phase for each alloy in the $\alpha + \sigma$ region was extrapolated along its tie line to locate a point at the boundary on the corresponding interplanar spacing contour. Using cobalt radiation, the diffraction line corresponding to the interplanar spacing (labeled 1 above) was perceptible, for alloys of the $\alpha + \sigma$ region, where the sigma phase comprised less than 10 per cent of the total alloy.

The contours shown in the signa region in Figs. 6 and 14 are indicated in terms of the length of the basal edge of the tentative tetragonal cell developed in Appendix III. This parameter was used only as a convenience to indicate the variation of the parameters of this phase.

As can be seen from either Fig. 6 or Fig. 14, the accuracy of the location of the boundary between the sigma region and the $\propto +\sigma$ region increases continuously with molybdenum content to a maximum accuracy near the sigma-apex of the three-phase $\propto + \varepsilon + \sigma$ triangle. For molybdenum contents less than approximately 25 per cent, the accuracy of the boundary determined by the X-ray method is poor. In this region microscopy was utilized.

The diffraction pattern of alloy No. 105 did not reveal the presence of the alpha phase in this alloy; however, the structure observed microscopically clearly indicated that the alloy was composed of two phases. A photomicrograph of this alloy is shown in Fig. 17a. A "scratch" test indicated that the darker constituent was softer than the clear etching sigma. Fig. 17b is a photomicrograph of alloy No. 20, which also would be interpreted to be one-phase sigma from diffraction data. Ferritic type grain boundaries may be observed in this structure. It was found that upon etching, the material at these boundaries was not attacked by the etchant. This material was left in relief and was interpreted to be alpha solid solution. Therefore, the phase boundary was so drawn to include these alloys in the $\ll + \sigma$ region. The lamellar structure

which may be seen in the photomicrograph of alloy No. 20 is of interest. This type structure was also observed in several alloys in the one-phase sigma region. A growth pattern of the sigma phase, which could produce such a structure, may be seen in the photomicrograph of alloy No. 105.

The attainment of equilibrium in alloys No. 21, 31, and 37, which are in the $\propto + \sigma$ region, is questionable. According to the phase boundaries shown in Fig. 6, the relative proportions of the sigma phase in these alloys should be of the order of 50, 25, and 75 per cent, respectively. X-ray diffraction patterns of these alloys showed very weak sigma lines and the structures observed microscopically would not indicate sigma to be in these proportions.

The equilibrium of the alloys in the $\propto +\sigma$ region in the Fe-Cr binary system is also questionable. The structure of alloy No. 62 indicated that this alloy consisted of one phase (alpha); however, very weak signa lines were observed in the diffraction pattern of this alloy. The structures observed microscopically in the rest of the alloys in this region of the ternary system were compatible with the derived phase boundaries.









Chromium.











Specimen No.: 120 (SOLID SOLUTION) (ALPHA) Composition: 52FE - 48CR Etch: Electrolytic, 10 % Oxalic Acid

Specimen No.: 120 (SIGMA) Composition: 52Fe - 48CR Etch: Electrolytic, 10 % Oxalic Acid

Figure 17

V. THE PHASE REGIONS: EPSILON, ALPHA PLUS EPSILON

AND ALTHA PLUS EPSILON PLUS SIGNA

The Fe-Mo binary system (Fig. 2) shows that the composition range of the epsilon phase is very marrow and that a true compound exists corresponding to the formula FegMo2. Since Arnfelt and Westgren (27) have determined the structure of the epsilon phase and associated the formula Fe_7Mo_6 with this structure, it was considered important to check the composition range of the epsilon phase in the Fe-Mo system.

Only diffraction lines characteristic of the epsilon structure were observed in the X-ray diffraction pattern of alloy No. 12 (60 Fe-40 Mo corresponding to FegMo₂). Data obtained from alloys No. 13 (59.9 Fe-46.1 Mo corresponding to FeqMo₈) and No. 14 (50 Fe-50 Mo) showed characteristic diffraction lines of the alpha phase. The spacings corresponding to high-angle reflections of the epsilon phase in these alloys were the same as those for alloy No. 12. Therefore, the composition corresponding to FegMo₂ is shown in Fig. 6 as one boundary of this phase.

Alloys Ho. 80 through 83 were investigated in an effort to determine the width of the fregion in the Fe-Mo binary system. The structure of alloy No. 80 when observed microscopically showed that this alloy consisted of two phases. In addition, interplanar spacings of the epsilon phase in these alloys were invariant. It was concluded that the range of composition over which epsilon exists in the Fe-Mo binary system is less than two atomic per cent.

This conclusion is in agreement with the composition limits shown in Fig. 2 for this phase.

The solubility of iron in molybdenum in the Fe-Mo binary system was determined by plotting the lattice parameters of alloys No. 48, 44, 45, 46, 48, and 50 versus composition as shown in Fig. 18. The phase boundary between the alpha region and the $\propto + \varepsilon$ region in the binary was fixed as shown in this figure.

The alloys in the three-phase $\propto + \epsilon + \sigma$ region are alloys No. 75, 76, 135-138, 153-159, 164, 166, and 167. The signa phase was observed in the diffraction patterns of alloys No. 75, 76, 135-138, 165-159, 164, 166, and 167. Epsilon was observed in diffraction patterns of alloys No. 136, 153-155, 164, 166, 167, and was questionable in the diffraction patterns of alloys No. 75 and 137. Alpha was clearly present in diffraction patterns of alloys No. 76, 137, 138, and 156-159.

The complicated pattern of epsilon superimposed upon the likewise complicated pattern of sigma (Fig. 8) presented a practical difficulty in the interpretation of the diffraction patterns of several of these alloys. Where only a small proportion of epsilon existed with a large proportion of sigma, or vice versa, it was difficult to ascertain the presence of the minor constituent. This difficulty was not too serious in view of the following considerations.

The alloys in which the signa phase was observed established the invariance of the interplanar spacings of the signa phase. The invariance of the interplanar spacings of the epsilon phase in alloys

where large proportions of this phase were present was also easily established. As can be seen from Table II, the lattice parameter of the alpha phase for alloys of this region is constant. Therefore, the criterion for a three-phase region is satisfied.

The boundary between the $\varepsilon + \propto$ region and the $\prec + \varepsilon + \sigma$ region was determined on the basis of alloys No. 156 and 164. These alloys are within one atomic per cent of the Fe-Mo binary system and contain three phases. Consequently, the boundary between the two-phase $\varepsilon + \propto$ region and the three-phase $\prec + \varepsilon + \sigma$ region is approximately parallel to the Fe-Mo binary system.

The location of the alpha-apex of the $\alpha + \varepsilon + \sigma$ triangle was determined from the intersection of the boundary between the $\varepsilon + \alpha$ and the $\alpha + \varepsilon + \sigma$ regions with the 3.125 Å alpha region lattice parameter contour. This value of the lattice parameter is representative of parameters of the alpha phase in alloys of the $\alpha + \varepsilon + \sigma$ region.

The location of the epsilon-apex of the $\prec + \varepsilon + \sigma$ triangle was determined on the basis of alloys No. 86, and 151 through 155, and on the basis of the boundary between the $\varepsilon + \alpha$ region and the $\alpha + \varepsilon + \sigma$ region. Alloys No. 153, 154, and 155 were located in the three-phase region (see above). Alloys No. 88 and 152 were located approximately on the same tie line in the $\varepsilon + \sigma$ region. The epsilon apex was found to be located at a composition of approximately 54 Fe - 1 Cr - 45 Mo. The boundary between the $\varepsilon + \alpha$ region and the $\alpha + \varepsilon + \sigma$ region determined the chromium content of this apex.

The tie line through alloys No. 88 and 152 determined the molybdenum content.

The boundary between the $\propto + \varepsilon + \sigma$ region and the $\propto + \sigma$ region was established on the basis of the alpha-apex of the three-phase region and the tie lines in the $\propto + \sigma$ region. This boundary in the ternary diagram was drawn from the alpha-apex. The slope of the boundary was adjusted so that the boundary was nearly parallel to the nearest tie line in the $\propto + \sigma$ region. The sigma end of this boundary was determined on the basis of the interplanar spacing contours in the one-phase sigma region. A straight line between this point and the composition limit of the one-phase epsilon region determined the boundary between the $\varepsilon + \sigma$ region and the $\propto + \varepsilon + \sigma$ region.



VI. PHASE BOUNDARIES IN THE IRON-RICH PORTION

OF THE TERNARY SYSTEM

The phase boundaries shown in the iron-rich portion of the ternary system were determined primarily by microscopy. As can be seen from the lattice parameter contours shown in the alpha prime (\prec') region (Fig. 6), the lattice parameters vary a small amount. Therefore, in order to establish accurate boundaries by the K-ray method, the accuracy of the lattice parameters should be greater than that attained in this investigation. In addition, a large number of alloys would be required to establish parameter contours in the one-phase \prec' region and tie lines in the adjacent two-phase regions. The lattice parameter contours shown in this region in Fig. 6 are only approximate and were determined by constructing lines through points of equal lattice parameter in the Fe-Cr and the Fe-Mo binary systems. The diffraction data for these binary systems were obtained with the large camera.

The solubility limit of molybdenum in iron (1200° F) in the Fe-Mo binary system was determined by X-ray diffraction in conjunction with microscopy. A plot of lattice parameter versus composition (Fig. 19) indicates that the solubility of molybdenum in iron in the binary system is four per cent. The photomicrograph of alloy No. 25 (Fig. 20b) shows this alloy to be composed of two phases with the second phase, \mathcal{E} , finely distributed within the grains. Fig. 20a shows that an alloy of two per cent molybdenum in the binary system is composed of one phase; therefore, the

boundary is at some composition between two and four per cent molybdenum. In view of the X-ray diffraction data, the boundary was located between three and four per cent molybdenum.

The phase boundaries in the vicinity of the \propto '-apex of the \propto '+ ε + σ region were determined solely by microscopy. The compositions of the alloys used for this investigation were determined after the boundaries had been approximately located on the basis of X-ray diffraction. In particular, the \propto '-apex of the three-phase triangle was located in the composition range enclosed by alloys No. 168 through 185. These alloys were then prepared for metallographic observation.

The boundary between the α' and $\alpha' + \varepsilon$ regions was located from the structures observed in alloys No. 168 and 169. The boundary was found to lie between one and two per cent molybdenum on the ten per cent chromium section. The structures observed are illustrated by photomicrographs of these alloys in Fig. 20c and Fig. 20d respectively.

The intersection of the boundary between the $\prec' + \varepsilon$ region and the $\prec' + \varepsilon + \sigma$ region with the ten per cent chromium section was established near nine per cent molybdenum. This intersection was established by microscopy in conjunction with X-ray diffraction. Photomicrographs of the alloys which were used in this determination are shown in Figs. 21a, 21b, and 21c. Alloy No. 16 (Fig. 21c) was found to contain three phases. This fact was determined from the X-ray diffraction pattern of this alloy. From Figs. 21b and 21c,

it appears that the sigma phase is present at the grain boundaries with the epsilon phase distributed within the grains in a matrix of the \propto phase. The structure of alloy No. 174 appears similar to the structure of alloy No. 175; however, the grain boundary precipitate is not well defined in alloy No. 174. Therefore, from microscopy alone, it cannot be concluded that the boundary is near the composition of nine per cent molybdenum. However, by considering the X-ray diffraction data of alloys in this composition range, it is estimated that the error is not larger than two per cent.

The boundary between the $\propto' + \varepsilon + \sigma$ region and the $\propto' + \sigma$ region was located near six per cent molybdenum along the 80 per cent iron section by considering the structures of alloys No. 178, 179, and 147. Photomicrographs of these alloys are shown in Fig. 21d, Fig. 22a, and Fig. 22b respectively. The structure of alloy No. 178 is assumed to consist of three phases with the sigma phase located at the grain boundaries and the epsilon phase distributed within the grains in a matrix of the \propto' phase. The photomicrograph of alloy No. 179 (Fig. 22a) presumably shows the sigma phase at the grain boundaries and Fig. 22b shows that the sigma phase is precipitated within grains of the \propto' phase. An X-ray diffraction pattern of alloy No. 147 showed vory weak lines of the sigma phase. From these considerations, it was concluded that the phase boundary between the $\propto' + \varepsilon + \sigma$ region and the $\propto' + \sigma$ region was near six atomic per cent molybdenum on the 80 per cent iron section.

The boundary between the $\propto' + \sigma$ region and the \propto' region was

determined from the structures observed in alloys No. 182 and 183. Photomicrographs of these alloys are shown in Figs. 22c and 22d respectively. These photomicrographs show that the boundary lies in the interval between one and two atomic per cent molybdenum along the 80 per cent iron section.

The boundary between the α' and $\alpha' + \sigma'$ regions in the Fe-Cr binary system is not considered accurate because the lattice parameter in the $\alpha' + \sigma'$ region of this ternary system is not a constant. The variation of the lattice parameter with composition in the Fe-Cr binary system is shown in Fig. 13. The boundary was approximately located by using information obtained from the diffraction pattern of alloy No. 59. Weak lines observed in this diffraction pattern were attributed to the presence of the sigma phase. However, the intensities of these lines were so weak that their interpretation was difficult. Therefore, the boundary between α' and $\alpha' + \sigma'$ in the binary system is questionable and the boundary between these two regions is shown as a dashed line in the vicinity of the Fe-Cr binary system in Fig. 6.

The alloys in the three-phase $a' + \epsilon + \sigma'$ region are alloys No. 16, 71, 72, 85, 86, 89, 91, 132, 133, 149, 176, 177, and 178. Alloys No. 176, 177, and 178 were analysed by microscopy only. The remainder of these alloys were found to be located in the threephase region by comparing parameters of the three individual phases. Here again, the superposition of complicated diffraction patterns was annoying. However, the parameters of the three separate phases

were determined by investigating regions of the three-phase triangle where only two phases were predominant. The \propto ' phase was clearly observed in alloys No. 16, 71, 85, 69-91, 152, 133, and 149. As can be seen from Table II, the lattice parameter of the body-centered-cubic phase of these alloys is constant within the limits of the experimental accuracy. Diffraction lines of the epsilon phase were observed in all of the alloys except alloy No. 91. Further, the interplanar spacings of epsilon in the threephase alloys were found to be nearly the same as those of alloy No. 12 (i.e. FegMo2). For this reason, the epsilon-apex of the threephase triangle was fixed as shown in Fig. 6. The line from this point intersecting the ten per cent chromium section at a composition of nine per cent molybdenum is then the boundary between the $\propto' + \varepsilon$ region and the $\prec' + \varepsilon + \sigma'$ region.*

The boundary between the $\prec' + \epsilon + \sigma'$ region and the $\prec' + \sigma'$ region was drawn so that it intersected the 80 per cent iron section at the composition of six per cent molybdenum. This boundary was drawn so that it included alloy No. 89 in the three-phase region and excluded alloy No. 56. Alloy No. 56 is in the $\prec' + \sigma'$ region. This was established by the interplanar spacings of the sigma phase of this alloy. The end-point of this boundary at the sigma-apex of the three-phase triangle was determined on the basis of the interplanar spacings of the sigma phase in three-phase alloys and on the basis of the interplanar spacing contours in the one-phase sigma region. A straight line drawn between this point and the point corresponding

to the epsilon-apex is then the boundary between the $\propto^{1} + \varepsilon + \sigma'$ region and the $\varepsilon + \sigma'$ region.

The phase boundary between the $\mathcal{E} + \sigma'$ region and the σ' region was drawn as a smooth curve between the sigma-apex of the $\alpha' + \mathcal{E} + \sigma'$ region and the sigma-apex of the $\alpha' + \mathcal{E} + \sigma'$ region. As can be seen from Fig. 6, the tie lines in the $\mathcal{E} + \sigma'$ region are very nearly parallel to the parameter contours in the one-phase sigma region. Therefore, the determination of this boundary by the intersection of tie lines with parameter contours was not possible. In addition, the alloys near the boundary between these regions were very porous. In the $\mathcal{E} + \sigma'$ region, none of the alloys were dense enough to give a satisfactory surface for etching. However, this boundary as drawn was substantiated by the two-phase alloys No. 92 and 93 and the onephase alloys No. 79 and 74.

The boundary between the σ region and the two-phase $\alpha' + \sigma'$ region is shown in Fig. 6. This boundary was established from the boundary between the $\alpha' + \sigma'$ region and the σ' region in the Fe-Cr binary system, from the sigma-apex of the $\alpha' + \varepsilon + \sigma'$ triangle determined above, and from the alloys in the $\alpha' + \sigma'$ region.

The boundary between the σ' region and the $\prec' + \sigma'$ region in the Fe-Cr binary system was determined on the basis of X-ray diffraction. The boundary between the $\prec' + \sigma'$ region and the σ' region was found to be located between 42 and 44 per cent chromium. This result agrees with the results of Cook and Jones shown in Fig. 1.

The structures observed microscopically in alloys No. 18, 56, 97, 98, and 100 showed that these alloys consisted of two phases. This result agrees with the X-ray diffraction data except for alloy No. 98. Ho body-centered-cubic phase could be detected from the diffraction pattern of this alloy. However, according to the boundaries shown in Fig. 6 for the $\propto' + \sigma'$ region the smount of the body-centered-cubic phase in this alloy should be less than two per cent. This was substantiated by the small amount of alpha prime observed in the structure of alloy No. 98.



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Specimen No.: 168 Composition: 89FE - 10CR - 1MO Etch: Electrolytic, 10 % Oxalic Acid

Specimen No.: 169 Composition: 88FE - 10CR - 2MC Etch: Electrolytic, 10 % Oxalic Acid

Figure 20



Specimen No.: 16 Composition: 80Fe - 10Cr - 10Mo Etch: Electrolytic, 10 % Oxalic Acid

Specimen No.: 178 Composition: 80Fe - 13CR - 7Mo Etch: Electrolytic, 10 % Oxalic Acid

Figure 21



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Etch: ELECTROLYTIC, 10 % OXALIC ACID

Etch: ELECTROLYTIC, 10 % OXALIC ACID

VII. ACCURACY OF RESULTS

The location of the phase boundaries shown in Fig. 8 are subject to the following sources of error:

- (1) Inaccuracies in the determination of lattice parameters and interplanar spacings.
- (2) Lack of equilibrium in alloys.
- (3) Actual composition of alloys compared with experimental composition shown in Fig. 7.

(1) The accuracy of the lattice parameters determined for the body-centered-cubic phases is discussed in Appendix II. The lattice parameters determined from data obtained with the small camera are accurate to within ± 0.002 Å. The accuracy of the interplanar spacings which were used to determine the boundaries of the sigma phase and the epsilon phase was of the same order of magnitude (Appendix II). As can be seen from Figs. 9, 11, 12, and 13, an error of 0.002 Å in the lattice parameter causes a composition error of approximately one per cent in the location of the lattice parameter points in Fig. 14. From Fig. 15 and Fig. 16, it can be seen that an error of 0.002 Å in the interplanar spacing (line Mo. 1) of the sigma phase also causes a composition error of one per cent. Therefore, the contours shown in Fig. 6 are considered accurate to within ± 1 atomic per cent.

(2) The sharpness of diffraction lines for high Bragg angles was used to determine the homogeneity existing in alloys after being aged for ten days at 1200° F. The sharpness of these diffraction

lines is a valid criterion for determining the existence of equilibrium because the widths of these diffraction lines are a measure of the consistency of the spacing between atomic planes. The lines obtained from the high angle reflections are sensitive to inhomogeneities in the lattice and to variation in phase composition.

It must be realized that the reaction rates which determine the approach to equilibrium at a particular temperature are a function of composition. A standard aging time may be sufficient to obtain equilibrium in some regions but may be insufficient in others. Sharp diffraction lines were obtained for the majority of the alloys. The apparent lack of equilibrium in alloys No. 21, 31, and 37 was discussed in Section IV. In addition to the above alloys, the equilibrium of alloys in the $\prec' + \sigma$ and $\prec + \sigma$ regions of the Fe-Cr binary system was also questioned. The phase boundaries in the vicinity of the Fe-Cr binary system are shown as dashed lines.

(3) The vapor pressure of pure ohromium is approximately $1 \ge 10^{-4}$ atmospheres at 2500°F and $1 \ge 10^{-13}$ atmospheres at 1200°F. It has been reported that in the alloyed state, the vapor pressure of chromium is lowered (30). Since chromium is quite volatile at 2500°F, it was necessary to determine whether or not the loss of chromium in the sintering process was excessive.

The loss of weight of an alloy of 52 Fe-48 Cr was found to be 0.11 per cent of the original weight after four hours sintering at 2500° F. If this loss of weight is assumed to be due only to the vaporization of chromium, the change in composition would be

approximately 0.03 atomic per cent.

In addition, two alloys which had been sintered for eight hours at 2500° F and had been aged for ten days at 1200° F were chemically analyzed by the Smith-Emery Co. of Los Angeles, California. These alloys were No. 91 and No. 101. The quantitative analysis is compared with the as mixed composition in weight per cent below:

| Alloy No. 91 | Weight per cent (Analysis) | (As mixed) |
|-----------------|-------------------------------|------------|
| | | |
| Carbon (C) | 0.06 | 60 G) |
| Iron (Fe) | 53.25 | 51.32 |
| Chromium (Cr) | 11.72 | 11.95 |
| Molybdenum (Mo) | 34.93 | 36.73 |

Alloy No. 101

| Carbon (C) | 0.03 | 4 49 |
|-----------------|-------|-------------|
| Iron (Fe) | 56.25 | 54.54 |
| Chromium (Cr) | 85.41 | 36.94 |
| Molybdenum (No) | 8.40 | 8.52 |

Traces of Ni, Cu, and Si.
On an atomic basis, the comparison of the analysis with the as mixed composition is as follows:

| Alloy No. 91 | Atomic per cent (Analysis) | Atomic per cent (As mixed) |
|-----------------|-------------------------------|-------------------------------|
| Carbon (C) | 0.32 | යා ක |
| Iron (Fe) | 61.60 | 60 |
| Chromium (Cr) | 14.56 | 15 |
| Molybdenum (Mo) | 23.52 | 25 |
| | | |

Alloy No. 101

| Carbon (C) | 0.14 | | 40 40 |
|-----------------|-------|-----|--------------|
| Iron (Fe) | 58.64 | | 55 |
| Chromium (Cr) | 58.29 | * x | 40 |
| Molybdenum (Mo) | 4.92 | | 5 |

It was stated by these chemists that their usual accuracy in a chemical analysis of this nature is of the order of ±2 per cent for a component which comprises 50 per cent of an alloy and ±1 per cent for a component which comprises 25 per cent. It was further stated that analysis for molybdenum in amounts greater than one per cent is difficult. A precision greater than the limits stated above was requested for the analysis of alloys No. 91 and 101. At extra cost, the results of two separate determinations on each of the alloys differed by a maximum of 0.53 per cent for an individual component. An average of the two determinations is presented above.

The loss of molybdenum in alloys No. 91 and 101 is not compatible with the vapor pressure of this metal compared with the vapor pressure of iron. The vapor pressure of molybdenum at 4160° F is 0.001 mm Hg and of iron at 3420° F is 1 mm Hg (31). Therefore, it appears that the analysis is in error due to the difficulty attending the determination of molybdenum. Further, the comparison of the results of the investigations of the binary systems for the three component metals with the results of previous investigators indicates that the composition accuracy is greater than that indicated from the analysis of alloys Nos. 91 and 101. The location of the epsilon phase in the Fe-Mo binary system and the solubility limits of iron in molybdenum and of molybdenum in iron in this system as determined by this study are compatible (at 1200° F) with the diagram shown in Fig. 2. The variation of lattice parameter with composition in the Cr-Mo system is compared with data presented by Trzebiatowsky (27) in Fig. 9. As shown, the agreement is good. Preston's data on the variation of lattice parameters with composition in the Fe-Cr system also agrees closely with the results shown in Fig. 10.

In view of the above discussion on the accuracy of the chemical analysis of alloys No. 91 and 101 and the agreement of the present results with data of previous investigators, it appears that the as mixed composition of alloys is reliable. It is estimated that the actual composition of the alloys is within one atomic per cent of the composition shown in Fig. 7. This error will have a minor effect

on the location of the phase boundaries.

It may be seen from the analysis of alloys No. 91 and 101 that some carbon is present in these alloys. Since these alloys received the maximum handling (i.e. crushing and resintering), it is assumed that the maximum amount of carbon present in any of the alloys prepared is of the order of 0.06 weight per cent. The alloys were not analyzed for oxygen content and it should be noted that oxygen may also be present in the form of Cr_2O_3 . Adcock (32) states that electrolytic chromium may contain from one to two per cent of this stable chromic oxide.

The carbon and oxygen present in alloys used in this investigation are not expected to have a serious effect on the phase boundaries. The presence of carbides or Cr20g was not detected microscopically or by X-ray diffraction.

In general, the shape of the phase boundaries shown in Fig. 6 is probably more correct than their absolute locations. A numerical calculation of the accuracy of the phase boundaries is impossible, but it is estimated that on the average they are accurate to within two atomic per cent.

VIII. DISCUSSION OF RESULTS

The ternary phase diagram of the Fe-Cr-Mo system as determined by the present investigation is shown in Fig. 6.

In the foregoing sections, the present results in the three binary systems have been compared with the results of previous investigators. The agreement is summarized as follows:

1. The phase boundaries of the sigma phase in the Fe-Cr binary system at 1200° F agree within one per cent with the boundaries determined by Cook and Jones (Fig. 1). After ten days at 1200° F, some of the alloys in the two-phase regions of this binary system were not considered to be in equilibrium. The boundary between the \propto' and the $\alpha' + \sigma'$ regions and the boundary between the α and the $\alpha' + \sigma'$ regions are not considered to be accurate. The data regarding the variation of lattice parameters with composition in this system (Fig. 10) agree within 0.001 Å with the data of Preston.

2. The phase boundaries in the Fe-Mo binary system at 1200° F agree within one per cent with the boundaries of this system at this temperature shown in Fig. 2.

3. The data on the variation of lattice parameters with composition in the Cr-Mo system (Fig. 9) agree closely with the data of Trzebiatowsky and colleagues. The maximum deviation in the two curves is 0.01 Å.

The only results available in the literature which may be compared with the phase boundaries determined for this ternary

system are given by Parke and Bens (9). These investigators state that the sigma phase was found in alloys in the composition range 60 Cr, 15-25 Fe, and 25-15 Mo (per cent by weight). The composition limit 60 Cr - 25 Fe - 15 Mo corresponds to 65.64 Cr - 25.47 Fe -8.89 Mo atomic per cent and lies well within the $\ll + \sigma$ region of Fig. 6. The composition limit 60 Cr - 15 Fe - 25 Mo (weight per cent) corresponding to 68.56 Cr - 15.96 Fe - 15.48 Mo atomic per cent, lies outside the two-phase region. This composition, however, is within one atomic per cent of the boundary between the $\ll + \sigma$ region and the \ll region of Fig. 6. In this composition range, the boundary is shown as a dashed line and the true boundary may well include this composition.

The apparent lack of equilibrium in several alloys after aging for ten days at 1200° F has been discussed previously. A compromise between inordinately long aging times and very short aging times is clearly necessary. In this investigation, all alloys were aged for ten days at 1200° F. Therefore, the diagram presented in Fig. 6 should be considered as the phase diagram for Fe-Cr-Mo alloys which have been aged for ten days at 1200° F.

IX. SUMMARY AND CONCLUSIONS

The phase boundaries of the iron-chromium-molybdenum ternary system at 1200° F have been investigated. The location of these boundaries (Fig. 6) was determined from an experimental investigation of 160 alloys. These alloys were aged for ten days at 1200° F. The experimental measurements were made by using the following techniques: X-ray diffraction, microscopy, and microhardness. It is estimated that the location of the phase boundaries is accurate to within two atomic per cent.

The necessity for the complementary use of X-ray diffraction and microscopy in an investigation of this nature has been clearly demonstrated.

It was found that the sigma phase of the Fe-Cr binary system is stabilized by the addition of molybdonum and that this brittle phase is present in a large portion of the ternary phase diagrams.

A tentative tetragonal structure for the sigma phase is developed in Appendix III. This structure is probably not the true structure of this phase. However, the predicted diffraction pattern of the tentative structure is so similar to the diffraction pattern of the sigma phase that this model is very convenient for correlation purposes.

Further basic research should be done on the segment of the boundary between the \propto and $\propto + \sigma$ regions which lies in the chromium-rich portion of the ternary system. This boundary should be determined as a function of temperature in order to establish

the useful composition range for gas turbine alloys. A knowledge of the extent of the sigma phase in this composition range could aid tremendously in the production of these high temperature alloys.

APPENDIX I

TABLE II

ALLOY COMPOSITIONS, THERMAL HISTORY, HARDNESS,

LATTICE PARAMETER-BCC PHASE, AND PHASE REGION OF ALLOYS

| Alloy No. | oy Composition Atomic Percent | | Thermal Hardness History Knoop No. | | Lattice Parameter | Region | |
|--------------|----------------------------------|------|---------------------------------------|------|----------------------|---------|---------|
| | Fe | Cr | Mo | | | a units | 1200° F |
| 1 | 0 | 8.9 | 91.1 | 3* . | - | 8.125 | × |
| 2 | 0 | 17.0 | 83.0 | 3* | - | 3.107 | X |
| 3 | 0 | 24.6 | 75.4 | 3** | - | 3.097 | ~ |
| 4 | 0 | 31.6 | 68.4 | 3** | - | 3.080 | × |
| 5 | 0 | 44.3 | 55.7 | 3** | - | 3.052 | ~ |
| 6 | 0 | 55.2 | 44.8 | 3** | - | 3.019 | 2 |
| 7 | 0 | 64.9 | 35.1 | 3** | - | 2.993 | X |
| 8 | 0 | 73.6 | 26.3 | 3** | | 2.964 | 8 |
| 9 | 0 | 81.2 | 18.8 | 3* | - | 2.936 | ~ |
| 10 | 0 | 88.1 | 11.9 | 3* | - | 2.918 | 8 |
| 11 | 0 | 94.5 | 5.5 | 3* | - | 2.903 | ~ |
| 12 | 60 | 0 | 40 | 2*** | - | ~ | ε |

*These alloys were sintered 12 hours at 2500° F.

**These alloys were crushed after sintering for four hours at 2500° F, re-pressed, and resintered for eight additional hours at 2500° F.

***Subsequent to the above alloys, (1) will identify an alloy that was sintered for four hours at 2500° F; (2) will identify alloys that were sintered four hours at 2500° F, crushed, re-pressed, and resintered for an additional four hours at 2500° F.

Subsequent to sintering, all alloys received ten days at 1200° F in vacuum followed by rapid cooling to room temperature.

| Alloy No. | Con Ator F e | aposit nic Po Cr | tion ercent Mo | Thermal History | Hardness Knoop No. | Lattice Parameter BCC Phase A units | Phase Region 1200° F |
|--------------|---------------------------|------------------------|----------------------|--------------------|-----------------------|--|----------------------------|
| 13 | 53.9 | 0 | 46.1 | 2 | - | 3.134 ₅ (L)*** | 3+>> ** |
| 14 | 50 | 0 | 50 | 2 | - | 3.135 ₂ (L) | \$ + E |
| 15 | 50 | 50 | 0 | 1 | - | - | б |
| 16 | 80 | 10 | 10 | 1 | 365 | 2.873 ₈ (L) | α+ε+σ |
| 17 | 70 | 20 | 10 | 1 | 505 | 2.874 ₂ (L) | a'+ 0 |
| 18 | 60 | 30 | 10 | 1 | 810 | 2.366 ₂ (L) ^a | x+0 |
| 19 | 50 | 40 | 10 | 1 | 1090 | | σ |
| 20 | 40 | 50 | 10 | 1 | 1130 | 2.906 | x + 0 |
| 21 | 30 | 60 | 10 | 1 | 540 | 2.910 | x + 0 |
| 2 2 | 20 | 70 | 10 | . 1 | 490 | 2.904 ₀ (L) | × |
| 23 | 10 | 80 | 10 | l | 550', | 2.907 ₆ (L) | ~ |
| 24 | 98 | 0 | 2 | l | 95 | 2.868 ₅ (L) | a' |
| 25 | 96 | 0 | 4 | 1 | 175 | 2.871 ₃ (L) | x'+E |
| 26 | 94 | 0 | 6 | 1 | 235 | 2.871 ₃ (L) | a'+E |
| 27 | 92 | 0 | 8 | 1 | 330 | 2.871 ₃ (L) | ≪'+E |
| 28 | 90 | 0 | 10 | 1 | 260 | 2.8718(L) | a'+E |
| 29 | 5 | 90 | 5 | 1 | 400 | 2.896 ₀ (L) | a |
| 30 | 15 | 70 | 15 | 1 | 455 | 2.923 ₉ (L) | × |
| 31 | 20 | 60 | 20 | 2 | 865 | 2.9417(L) | x+0 |

****(L) Identifies parameters determined from data obtained using the 214.86 mm camera.

a Probably not in equilibrium.

| Alloy No. | Comp Atomi | ositi Lo Pero | on cent | Thermal History | Hardness Knoop No. | Lattice Parameter | Phase Region |
|--------------|---------------|------------------|--------------|--------------------|-----------------------|----------------------|-------------------|
| | Fe | Cr | Мо | | | A units | 12000 F |
| 32 | 25 | 50 | 25 | 2 | 540 | 2.956 | a+0 |
| 33 | 40 | 40 | 20 | 2 | 1060 | - | б |
| 34 | 35 | 85 | 30 | 2 | - | ~ | σ |
| 35 | 45 | 45 | 10 | 1 | 915 | | б |
| 36 | 47.5 | 47.5 | 5 | 1 | 1075 | 66 | σ |
| 37 | 30 | 55 | 15 | 1 | 455 | 2.912 | a+ob |
| 38 | 5 | 80 | 5 | 2 | 590 | 2.928 | X |
| 39 | 7.5 | 70 | 22.5 | 2 | 460 | 2.947 | ∝ |
| 40 | 10 | 60 | 30 | 2 | 635 230 | 2.968 | ∝+0 |
| 41 | 12.5 | 50 | 3 7.5 | 2 | 495 | 2.997 | x+0 |
| 42 | 15 | 40 | 45 | 2 | 505 | 2.017 | $\alpha + \sigma$ |
| 43 | 2 | 0 | 98 | 1 | 335 | 3.144 | α |
| 44 | 4 | 0 | 96 | 1 | 282 | 3.140 | X |
| 45 | 6 | 0 | 94 | 1 | 315 | 3.136 | X |
| 46 | 8 | 0 | 92 | 1 | 405 | 3.130 | ≪ + E |
| 47 | 10 | 0 | 90 | 1 | 465 | - | x + E |
| 48 | 12 | 0 | 88 | 1 | 425 | 3.130 | a + E |
| 49 | 14 | 0 | 86 | 1 | 465 | CR | X + E |
| 50 | 16 | 0 | 84 | 1 | 440 | 3.131 | α ,+ ε |
| 51 | 49.5 | 49.5 | 1 | 1 | 1020 | - | Ġ |
| 52 | 49 | 49 | 2 | 1 | 1070 | Ce | σ |
| | | | | | | | |

b Probably not in equilibrium, O very very weak.

| Alloy No. | Con Ator | apositi nic Per | on cent | Thermal Eistory | Hardness Xnoop No. | Lattice Phase Parameter Region RCC Phase 12000 F | | |
|--------------|-------------|--------------------|------------|--------------------|-----------------------|--|---------------------|--|
| | Fe | Cr | No | | | A units | 1200 ° F | |
| 53 | 48.5 | 48.5 | 3 | 1 | 945 | - | σ | |
| 54 | 48 | 48 | 4 | 1 | 880 | - | б | |
| 55 | 49.75 | 49.75 | 0.5 | 1 | 1045 | - | σ | |
| 56 | 60 | 20 | 20 | 1 | 1010 | 2.870 | x'+ 0 | |
| 57 | 90 | 10 | 0 | . 1 | 95 | 2.8704(L | j d' | |
| 5 8 | 80 | 20 | 0 | 1 | 120 | 2.872 ₁ (L |) «΄ | |
| 59 | 70 | 30 | 0 | 1 | 153 | 2.873 ₂ (L |) «'toc | |
| 60 | 60 | 40 | 0 | 1 | 220 | 2.8745 (1 | L) x'+ 0 | |
| 61 | 40 | 60 | 0 | 1 | 350 | 2.876 ₇ (L |) a+o | |
| 62 | 30 | 70 | 0 | 1. | 330 | 2.877 ₉ (L |) a+0 ⁰ | |
| 63 | 20 | 80 | 0 | 1 | 400, | 2.879 ₉ (L |) ~ | |
| 64 | 10 | 90 | 0 | 1 | 364 | 2. 889 ₉ () | L) X | |
| 65 | 30 | 30 | 40 | 2 | ** | - | σ | |
| 66 | 25 | 25 | 50 | 2 | - | 3.082 ₆ (L |) | |
| 67 | 20 | 20 | 60 | 2 | 500 | 2.093 ₈ (L | $) \propto +\sigma$ | |
| 68 | 15 | 15 | 70 | 1 | 470 | 3.103 | a + 0 | |
| 69 | 10 | 10 | 80 | 1 | 360 | 3.107 | x + 0 | |
| 70 | 5 | 5 | 90 | 1 | 365 | 3.122 ₁ (L |) ato | |
| 71 | 70 | 10 | 20 | 1 | 815 | 2.871 | x'+E+0 | |
| 72 | 60 | 10 | 30 | 2 | 790 | - | x'+E+0 | |
| | | | 14 | | | | | |

o Sigma questionable - very very weak.

| Alloy No. | Com Atom | positi ic Per | on cent | Thermal History | Hardness Knoop No. | Lattice Parameter BCC Phase | Phase Region |
|--------------|-------------|------------------|------------|--------------------|-----------------------|-----------------------------------|-------------------|
| | Fe | Cr | No | | | A units | 1200 F |
| 73 | 50 | 10 | 30 | 2 | - | ¢ij | ε+σ |
| 74 | 40 | 20 | 40 | 2 | aa | - | σ |
| 75 | 40´ | 10 | 50 | 2 | - | 4 2 | x+E+0 |
| 76 | 30 | 10 | 60 | 2 | 385 | 3.122 | x +E+J |
| 77 | 20 | 10 | 70 | 1 | 730 | 3.121 | $\alpha + \sigma$ |
| 78 | 50 | 30 | 20 | 2 | ~ | - | σ |
| 79 | 50 | 20 | 30 | 2 | - | - | σ |
| 80 | 62 | 0 | 38 | 2 | 980 | 2.871 | ≪'+E |
| 81 | 64 | 0 | 36 | 2 | en ' | 2.870 | α'+٤ |
| 82 | 66 | 0 | 34 | 2 | - | 2.868 | x'+E |
| 83 | 68 | 0 | 32 | 2 | 905 | 2.872 | α'+ε |
| 84 | 70 | 5 | 25 | 1 | 555 × _ | 2.872 ₇ (L |) ∝'+E |
| 85 | 65 | 5 | 30 | 2 | - | 2.870 | a'+E+0 |
| 86 | 60 | 5 | 35 | 2 | 870 | - | a'+E+0 |
| 87 | 55 | 5 | 40 | 2 | 495 | - | E+O |
| 88 | 50 | 5 | 45 | 2 | - | - | E+0 |
| 89 | 75 | 15 | 10 | 1 | 475 | 2.872 | x'+E+O |
| 90 | 70 | 15 | 15 | 1 | 760 | 2.871 | x'+E+0 |
| 91 | 60 | 15 | 25 | 2 | 9.5 | 2.073 | x'+E+0 |
| 92 | 50 | 15 | 3 5 | 2 | - | - | E+0 |
| 93 | 40 | 15 | 45 | 2 | - | - | ε+σ |
| 94 | 30 | 15 | 55 | 2 | 400 | 3.104 | $\alpha + \sigma$ |

| Alloy No. | Composition Atomic Percent | | on cent | Thermal History | Thermal Hardness History Knoop No. | | Phase Region 1200° F |
|--------------|-------------------------------|------|------------|--------------------|---------------------------------------|------------------------|----------------------------|
| | Fe | C.:- | Mo | | | A units | 1000 1 |
| 95 | 30 | 20 | 50 | 2 | 470 | 3.094 | a+0 |
| 96 | 17.5 | 17.5 | 65 | 2 | 425 | 3.096 | a +0 |
| 97 | 60 | 25 | 15 | 1 | 870 | 2.872 ₃ (L) | ≪'+ <i>σ</i> |
| 98 | 55 | 25 | 2 0 | 1 | 485 | 2.872 ₈ (L) | a'+o |
| 99 | 46 | 25 | 30 | 2 | | a | σ |
| 100 | 60 | 35 | 5 | 1 | 885 | 2.86 6 d | α'+σ |
| 101 | 55 | 40 | 5 | 2 | | | σ |
| 102 | 55 | 35 | 10 | 1 | - | ** | σ |
| 103 | 40 | 55 | 5 | 1 | 590 | 2.890 | a+0 |
| 104 | 35 | 55 | 10 | 1 | 630 | 2.910 | ato |
| 105 | 30 | 45 | 25 | 2 | 385 410 | - | $\alpha + \sigma$ |
| 106 | 25 | 40 | 35 | 2 | 520×_ | 3.001 | a +0 |
| 107 | 20 | 35 | 45 | 2 | 585 | 5.031 | ≪ + σ |
| 108 | 15 | 30 | 55 | 2 | 640 | 3.050 | x + 0 |
| 109 | 10 | 25 | 65 | 2 | 585 | 3.072 | x + 0 |
| 110 | 5 | 20 | 75 | 2 | 365 | 3.090 | a+0 |
| 111 | 0 | 10 | 90 | 2 | 220 | 3.126 | X |
| 112 | 0 | 20 | 80 | 2 | 345 | 3.103 | X |
| 113 | 0 | 30 | 70 | 2 | 530 | 3.080 | X |
| 114 | 0 | 40 | 60 | 2 | 525 | 3.059 | × |
| 115 | 0 | 50 | 50 | 2 | 520 | 3.034 | × |

d Parameter inaccurate due to very weak BCC lines.

| Alloy No. | Composition Atomic Percent | | Thermal History | Hardness Knoop Nc. | Lattice Parameter BCC Phage | Phase Region | |
|--------------|-------------------------------|------------|--------------------|-----------------------|-----------------------------------|-----------------|-------------------|
| | Fo | Cr | Ho | | | A units | 1200° F |
| 116 | 0 | 60 | 40 | 2 | 525 | 3.007 | \propto |
| 117 | 0 | 70 | 30 | 2 | 280 | 2.976 | × |
| 118 | 0 | 80 | 20 | 2 | 385 | 2.940 | X |
| 119 | 0 | 90 | 10 | 2 | 377 | 2.917 | X |
| 120 | 52 | 48 | 0 | 1 | | 6 2 | 0 |
| 121 | 54 | 46 | 0 | 1 | - | - | σ |
| 122 | 56 | 44 | 0 | 1 | - | - | σ |
| 123 | 58 | 42 | 0 | 1 | - | 2.876 | x'+0 |
| 124 | 62 | 38 | 0 | 1 | - | 2.876 | x'+0 |
| 125 | 65 | 35 | 0 | 1 | - | 2.870 | x'+0 |
| 126 | 48 | 5 2 | 0 | 1 | | 2.876 | a + 0° |
| 127 | 46 | 54 | 0 | 1 | • · · | 2.875 | x + 0° 0 |
| 128 | 44 | 56 | 0 | 1 | - | 2.874 | X + C 0 |
| 129 | 42 | 58 | 0 | 1 | - | 2.875 | x + 0 8 |
| 130 | 10 | 35 | 65 | 2 | 1110 | 3.034 | $\alpha + \sigma$ |
| 131 | 10 | 45 | 45 | 2 | 705 | 3.010 | x+J |
| 132 | 65 | 15 | 20 | 1 | 925 | 2.870 | x'+E+0 |
| 133 | 65 | 10 | 25 | 1 | 915 | ſ | x'+E+0 |
| 134 | 45 | 10 | 45 | 2 | 760 | - | EtOB |

e Probably not in equilibrium - however, σ observed.

f BCC phase observed very weak.

g Very weak Sigma lines superimposed on strong complicated Epsilon pattern, possibly not in equilibrium.

| Alloy | No. (At | Composition Atomic Percent | | Thermal History | Hardness Knoop No. | Lattice Parameter BCC Phase | Phase Region ' 1200° F |
|-------|-------------|-------------------------------|-----|--------------------|-----------------------|-----------------------------------|------------------------------|
| | Fe | o Cr | Mo | | | A units | 1000 1 |
| 135 | 38 | 10 | 55 | 2 | 620 | - | x+E+0 |
| 136 | - 45 | 5 5 | 50 | 2 | - | - | X+E+0 |
| 187 | 38 | 5 5 | 60 | 2 | 385 | 8.125 | x + E + O |
| 138 | 30 |) 5 | 65 | 2 | 350 | 3.124 | x + E + O |
| 139 | 38 | 5 15 | 50 | 2 | - | | $\alpha + \sigma$ |
| 140 | ŧ | 5 10 | 85 | 2 | 365 | 3.109 | d + 0 |
| 141 | £ | 5 30 | 65 | 2 | 520 | 3.058 | x +0 |
| 142 | 6 | 5 40 | 55 | 2 | 385 | 5.033 | a +0 |
| 143 | E | 5 50 | 45 | 2 | 410 | 3.010 | a +0 |
| 144 | 8 | 5 60 | 35 | 2 | 275 | 2.982 | × |
| 145 | ŝ | 5 70 | 25 | 2 | 510 | 2.955 | × |
| 146 | 88 | 5 10 | 5 | 1 | 310 ', | 2.872 | x'+E |
| 147 | 80 |) 15 | 5 | 1 | 360 | 2.874 | a'+0 |
| 148 | 78 | 5 20 | 5 | 1 | 315 | 2.871 | x'+ 0 ' |
| 149 | 621 | 5 2.5 | 35 | 1 | 490 | 2.874 | a'+E+0 |
| 150 | 60 | 2.5 | 37. | 5 2 | - | | 8+0 |
| 151 | 57 | 5 2.5 | 40 | 2 | - | ** | E+0 |
| 152 | 5 | 5 2.5 | 42. | 5 2 | - | - | E+0 |
| 153 | 52 | .5 2.5 | 45 | 2 | - | - | x + € + 0 |
| 154 | 50 | 2.5 | 47 | 5 2 | | - | X + E + O |
| 155 | 47 | .5 2.5 | 50 | 2 | - | - | α + ε + σ |
| 156 | 30 | 1 | 69 | 2 | - | 3.126 | x + E + O |
| 157 | 30 | 2 | 68 | 2 | - | 3.124 | $\alpha + \epsilon + \sigma$ |

| Alloy No. | Com Atom | Composition Atomic Percent | | Thermal History | Hardness Knoop No. | Lattice Parameter BCC Phase | Phase Region |
|--------------|-------------|-------------------------------|------------|--------------------|-----------------------|-----------------------------------|--------------------|
| | Fe | Cr | No | | | A units | 1200 F |
| 158 | 30 | 3 | 6 7 | 2 | 008 | 3.124 | x+E+0 |
| 159 | 30 | 4 | 66 | 2 | 515 | 3.124 | X + E + O |
| 161 | 2 | 20 | 79 | 2 | - | 3.090 | $\propto + \sigma$ |
| 162 | 2 | 30 | 68 | 2 | - | 3.064 | a + 0 |
| 164 | 45 | 1 | 54 | 2 | - | | a + E + O |
| 166 | 45 | 3 | 52 | 2 | - | - | x + E + O |
| 167 | 45 | 4 | 51 | 2 | - | - | x + E + O |
| 168 | 89 | 10 | 1 | 1 | - | h | م ′ |
| 169 | 88 | 10 | 2 | 1 | - | h | a '+E |
| 170 | 87 | 10 | 3 | 1 | - | h | x'+E |
| 171 | 86 | 10 | 4 | 1 | - | h | α'+ε |
| 172 | 84 | 10 | 6 | 1 | •• | h | a'+E |
| 173 | 83 | 10 | 7 | 1 | | h | \$`+E |
| 174 | 82 | 10 | 8 | 1 | ۶. • | h | ≪´+E |
| 175 | 81 | 10 | 9 | 1 | - | h | x'+E+0 |
| 176 | 80 | 11 | 9 | 1 | - | h | x'+E+0 |
| 177 | 80 | 12 | 8 | 1 | - | h | d + E + 0 |
| 178 | 80 | 13 | 7 | 1 | - | h | «'+ ε+ σ |
| 179 | 80 | 14 | 6 | 1 | - | h | x'+ o |
| 180 | 80 | 16 | 4 | 1 | | h | x'+J |
| 181 | 80 | 17 | 3 | 1 | - | h | x'+0 |
| 182 | 80 | 18 | 2 | 1 | | ĥ | x' + o |
| 183 | 80 | 19 | 1 | 1 | | h | Χ |

h Analyzed by microscopy only.

APPENDIX II

INVESTIGATION OF ERHORS INHERENT IN THE USE OF PONDER CAMERAS

The determination of interplanar spacings and lattice parameters by the use of a powder diffraction camera is subject to inherent systematic errors. These errors are due to film shrinkage, eccentricity of the specimen relative to the axis of the camera, and absorption of X-rays in the specimen. In addition, the measurement of the position of the diffraction line or the reflection angle is subject to a random error.

A correction was made for the film shrinkage by assuming that the shrinkage was uniform along the length of the film. Hence the data were assumed to be free from errors arising from this source. It was also assumed that the axis of rotation of the specimen coincided with the axis of the camera. The data showed that these two assumptions were valid.

The remaining errors are the systematic error due to absorption and the random error in reading the position of a diffraction line.

The fundamental interplanar spacing error equation may be developed directly from the Bragg law

$$n\lambda = 2dsin\theta$$
 (1)

The spacing, d, is computed from a measurement of Θ by using the equation

$$d = n\lambda/2 x \cos \theta .$$
 (2)

By differentiating equation (2), the fundamental error equation is

 $\Delta d = -(n \sqrt{2}) \times \csc \Theta \times \cot \Theta \times \Delta \Theta .$ (3)

To avoid confusion, Δ is used to indicate the differential quantities.

Dividing equation (3) by equation (2), the fractional error equation is

$$\Delta d/d = -\cot \Theta x \Delta \Theta \tag{4}$$

The lattice parameter, a, of a cubic structure is given by the relation a • $d\sqrt{h^2 + k^2 + l^2}$, where h, k, and l are the Miller indices of the atomic plane which corresponds to d. Therefore, the fractional error in the lattice parameter may be written as

$$\Delta a/a = -\cot \Theta x \Delta \Theta \tag{5}$$

A. Error in Reading Diffraction Film.

The source of the reading error may be seen from Fig. 5, where the position, x, of the diffraction line is subject to an error Δx . The error in Θ is then

$$\Delta \Theta = \pm \Delta x/2R \tag{6}$$

where R is the radius of the camera. This error for the small camera is shown in Fig. 23 where Δd is plotted versus d for the three radiations used in this investigation. The reading error curves for the large camera may be deduced from Fig. 23 by dividing the ordinates by three.

B. Absorption Error.

The absorption error arises, as shown below, from absorption of X-rays in the specimen.



This error is a function of the diameter of the specimen, the composition of the specimen, and the radiation employed. The observed Bragg angle is always larger than the true value. Therefore, the computed interplanar spacing, d, or the lattice parameter, a, will be biased in the negative sense.

For complete absorption in the specimen, i.e., reflection from atomic planes at the surface of the specimen only, Bradley and Jay (33) have shown this error to be related to an error in Θ by the formula

$$\Delta \Theta = \frac{r}{R} (1 + \frac{R}{Mx}) \cos^2 \Theta$$
 (7)

where r is the radius of the specimen, R is the radius of the camera, and Mx is the distance from the source of the X-ray beam to the specimen. The fact that the usual X-ray beam is slightly di-vergent is accounted for by the factor Mx. The coefficient of $\cos^2\theta$ in this equation will vary from specimen to specimen because

of an unavoidable variation in the radii of the specimens. However, this coefficient is constant for any one particular film. Therefore, the absorption error is written

$$\Delta \Theta = D \cos^2 \Theta \tag{8}$$

This equation substituted in (4) or (5) shows that errors of this nature vanish for $\theta = 90$ degrees. The function $\cos^2\theta$ has been used graphically by many investigators for extrapolating apparent values of the lattice parameter, a, to $\theta = 90$ degrees and thereby eliminating this error. The above technique, though derived for complete absorption in the specimen, has been shown to provide a satisfactory correction for values of the Bragg angle, θ , greater than 60 degrees.

In an excellent paper, M. U. Cohen (34) presented a very general analytical method for the determination of lattice parameters which has been used extensively in this country.

For cubic orystals, the Bragg equation can be expressed by the relation

$$(\lambda/2a_0)(h^2 + k^2 + 1^2)^{\frac{1}{2}} = \sin \theta_{hkl}$$
 (9)

where a_0 is the true lattice parameter and θ_{hkl} is the true Bragg angle for a particular plane, (hkl). Squaring both sides and denoting $\lambda^2/4 a_0^2$ by A_0 ,

$$A_{o}(h^{2}+k^{2}+1^{2}) = \sin^{2} \theta_{hkl}$$
 (10)

Expanding $\sin^2 \theta$ in a Taylor's series and substituting the series in equation (10), the following relation is obtained.

$$A_{0}(h^{2} + k^{2} + 1^{2}) = \sin^{2} \Theta i - \sin^{2} \Theta_{hkl} \triangle \Theta$$
(11)

where Θ i is the measured Bragg angle for a particular plane. Using Θ i for the true Bragg angle in Sin 2 Θ_{hkl} and substituting Bradley and Jay's absorption error for $\Delta \Theta$, equation (11) may be written as

$$\sin^2 \Theta \mathbf{i} = \mathbf{A}_{\mathbf{p}} \propto \mathbf{i} + \mathbf{D} \, \delta \mathbf{i} \tag{12}$$

where

$$A_{o} = \frac{\lambda}{4a_{o}^{2}}$$

$$\propto_{i} = (h^{2} + k^{2} + l^{2}) \text{ for the ith plane}$$

$$\delta_{i} = \cos^{2}\theta_{i} \sin^{2}2\theta_{i}$$

D = a constant depending upon absorption.

The usual equations which are used to solve this set of linear equations for A_0 are:

$$\sum_{i=1}^{N} \alpha_{i} \sin^{2} \theta_{i} = A_{0} \sum_{i=1}^{N} \alpha_{i}^{2} + D \sum_{i=1}^{N} \alpha_{i} \delta_{i}$$
(13)
$$\sum_{i=1}^{N} \delta_{i} \sin^{2} \theta_{i} = A_{0} \sum_{i=1}^{N} \alpha_{i} \delta_{i} + D \sum_{i=1}^{N} \delta_{i}^{2}$$

The above method was applied to small camera diffraction records for pure annealed iron, chromium, and molybdenum. The resulting values for the lattice parameters, utilizing only reflections for which $\Theta > 60$ degrees, are Fe, a = 2.866g Å, Cr, a = 2.884g Å, and Mo, a = 3.145g Å. These compare well with corresponding large camera determinations: Fe, a = 2.8662 Å, Cr, a = 2.8845 Å, and Mo, a = 3.1464 Å.

The coefficient of the absorption error in $\triangle \Theta$ was also computed for the small camera records of these pure metals. The percentage error in measured spacing, d, or lattice parameter, a, for these three records is plotted as a function of Θ in Fig. 24. These records were taken with cobalt radiation. For Co K₄₁ radiation, the mass absorption coefficient, P/ρ , for iron is approximately 58, for chromium is approximately 385, and for molybdenum is approximately 245. These values were determined by graphical interpolation of mass absorption coefficients given by Barrett (1). It can be seen from Fig. 24 that the absorption errors for the three specimens vary as expected with their relative mass absorption coefficients. Another error caused by the difference in radii of the three specimens may also be superimposed on the absorption error. This figure is intended to give only a relative idea of the error in the interplanar spacings which are caused by absorption. As the composition of the alloys is varied, the absorption error also varies. The curve for pure molybdenum may be used as an average.

The calculation of lattice parameters by Cohen's method is used extensively in this country for precise work on standard substances. However, for a systematic study of a large number of alloys, the method is not desirable because of the long and involved calculations required. For this investigation, these tedious calculations were not warranted, and a simpler graphical method was used for the elimination of the absorption error.

The lattice parameters, a, for the body-centered-cubic solid solution phase were corrected for absorption errors by the use of a graphical extrapolation technique which was recently suggested by Nelson and Riley (35). These authors investigated various functions of θ for use as extrapolation functions and showed empirically that

absorption errors are proportional to a function $F(\Theta)$ which equals $\cos^2\Theta/\sin\Theta + \cos^2\Theta/\Theta$. A plot of $\frac{1}{2}F(\Theta)$ versus apparent values of "a" was shown to be linear for values of $\Theta>30^{\circ}$. This extrapolation function was subsequently given a semi-theoretical basis by A. Taylor and H. Sinclair (36).

Using a table of $\frac{1}{2}F(\Theta)$, the apparent lattice parameters, a, of the body-centered-cubic phase were extrapolated to Bragg angle $\Theta = 90$ degrees. Examples of the use of this extrapolation function for several Fe-CrMo alloys are shown in Fig. 25. As can be seen from this figure, the linear relationship between apparent lattice parameters and $\frac{1}{2}F(\Theta)$ is very good.

It is interesting to note that if the lattice parameter, a, (computed from a particular plane (hkl) and for several alloys) is plotted versus $F(\Theta)$, the resulting curves are approximately straight lines (Fig. 25). This is an approximation for the small range of lattice parameters covered in this figure. The significance of this result is not understood.

The lattice parameters of the body-centered-cubic phase was corrected by the above method. This data was obtained with the small camera and is estimated to be accurate to within 0.002 Å. The lattice parameters which were determined from data taken with the large camera were not corrected for absorption. However, only high Bragg angle reflections were used for these calculations. It is estimated that these lattice parameters are accurate to within 0.0007 Å.

The variation with composition of the parameters of the sigma

and epsilon phases was determined from interplanar spacings. Diffraction lines in the back reflection range, i. e. $\Theta\rangle$ 60°, were used for these calculations. For the sigma phase, the interplanar spacings which were utilized were found to vary with composition from approximately 0.900 Å to 1.030 Å. These spacings were not corrected for absorption and the reading error is present. However, as can be seen from Fig. 23 and 24, the reading error and absorption error in this range ($\Theta\rangle$ 60°) are small. The maximum error in these interplanar spacings is estimated to be 0.002 Å.







APPENDIX III

TENTATIVE STRUCTURE FOR THE SIGMA PHASE

An investigation was made to determine if the structure of the sigma phase is hexagonal or tetragonal. Hull-Davey charts* were used in the attempt to establish the crystal structure. The best match of observed interplanar spacings with allowable spacings for a given structure was found on the tetragonal chart near an axial ratio, c/a = 1.46. The diffraction lines of the sigma phase were then assigned Miller indices as determined by this match and the best c/a ratio was determined by applying the least square method to the tetragonal formula.

The tetragonal formula is

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{1^2}{o^2}$$
(1)

or

$$1 = \frac{1}{a^2} (h^2 + k^2) d^2 + \frac{1}{o^2} 1^2 d^2 = AX + BY$$

where

$$X = (h^2 + k^2)d^2$$
$$Y = 1^2d^2$$
$$A = 1/a^2$$
$$B = 1/a^2$$

The above equation is that of a straight line. The intercepts of this line determine the value of a and c.

The sum of the squares of the orthogonal deviations are minimized. *For examples of Hull-Davey charts, see Reference 37. The procedure is as follows: Take $y_i^* = mx_i^* + b$ where m and b are constants to be determined in such a way that the sum of the squares of the orthogonal deviations of the data from the straight line is minimized. The orthogonal deviations are

$$\chi_{i} = (y_{i} - y_{i}^{*}) \frac{1}{\sqrt{1 + m^{2}}}$$
 (2)

or

$$X_{i} = [y_{i} - (mx_{i} + b)] \frac{1}{\sqrt{1 + m^{2}}}$$
.

Denoting the sum of the squares of the orthogonal deviations by F(m,b) we have

$$F(m,b) = \sum_{i=1}^{n} \left[\sqrt{y_i} - (mx_i + b) \right]^2 \frac{1}{1 + m^2}$$
(3)

Then minimizing

and

$$\frac{\partial F}{\partial m} = 0$$
(4)

The following two equations are obtained from equation (4):

$$\sum_{i=1}^{n} [y_{i} - (mx_{i} + b)] = 0$$
(5)
$$(1 + m^{2}) \sum_{i=1}^{n} x_{i} [y_{i} - (mx_{i} + b)] + m \sum_{i=1}^{n} [y_{i} - (mx_{i} + b)]^{2} = 0$$
(6)

Substituting the value of b from equation (5) in equation (6), the following equation for the determination of the slope, m, results:

$$m^{2} - \frac{N\left(\sum_{i=1}^{N} x_{i}^{2} - \sum_{i=1}^{N} y_{i}^{2}\right) - \left(\sum_{i=1}^{N} x_{i}\right)^{2} + \left(\sum_{i=1}^{N} y_{i}\right)^{2}}{\left(\sum_{i=1}^{N} x_{i}\right)\left(\sum_{i=1}^{N} y_{i}\right) - N\sum_{i=1}^{N} x_{i}y_{i}}$$
(7)

One root of this equation is the slope of the desired line. The

other root is the slope of the line for which the sum of the squares of the orthogonal deviations is a maximum.

Having the desired slope, m, the value of the constant b is found from equation (3) which reduces to

$$b = \frac{\sum_{i=1}^{N} y_{i} - m \sum_{i=1}^{N} x_{i}}{N}$$
(8)

The above formulas were applied to the best available diffraction pattern. A diffraction pattern of alloy No. 121 in the Fe-Cr binary was used. For interplanar spacings lower than approximately 1.6 Å, Miller indices could not be assigned to the observed diffraction lines. The proximity of the allowable spacings prevented a reliable indexing. Therefore, these interplanar spacings could not be utilized. Interplanar spacings corresponding to seventeen diffraction lines were utilized for the determination of the c/a ratio.

Fig. 26 is a plot of $x = d^2(h^2 + k^2)$, $y = d^2 l^2$ for these seventeen diffraction lines. The line for which the sum of the squares of the orthogonal deviations is minimum results in a c/a ratio of 1.461. The parameter, a for this cell was found to be 6.205 Å.

The quadratic form in $\sin^2\theta$ was established using the parameters of this cell. The computed values of $\sin^2\theta$ are compared with the observed values in Table III. The variation of $\sin^2\theta$ which might be expected from the reading error is of the order of ± 0.0005 .

Although no great difference exists between calculated and observed values of $\sin^2\theta$, the agreement is only fair. This result indicates that the assumed structure is not the true structure of this phase. It is interesting to note that the axial ratio 1.46 is nearly the $\sqrt{2}$, which means that a slightly distorted cubic cell might also describe the structure.

If it is assumed that the tetragonal cell described above is correct, the number of atoms per unit cell may be computed. It was found that the density of the Fe-Cr sigma phase is 7.600 ± 0.005 gm/cc. From this figure and the cell parameters, the number of atoms per unit cell was found to be 29.7, i.e. nearly 30 atoms.

The lattice parameters, a, of this tentative tetragonal cell for alloys in the sigma region were computed using the formula

 $a = d(h^2 + k^2 + 1^2/(1.461)^2)^{\frac{1}{2}}$

Values of $(h^2 + k^2 + 1^2/(1.461)^2)^{\frac{1}{2}}$ were tabulated and the lattice parameter, a, was computed for alloys in the sigma region. An average lattice parameter was computed from ten interplanar spacings.

The variation of the lattice parameter, a, with molybdenum content for the section where iron and chromium are in equal proportions is shown in Fig. 27. A similar variation for a section of constant iron (50 per cent) is also shown in Fig. 27. The variation of the interplanar spacings (Figs. 15 and 16) with molybdenum content is similar to the variation of the lattice parameter with molybdenum content.

The parameter contours shown in the sigma region of Fig. 6 indicate the variation with composition of the parameter, a, for the tentative tetragonal cell developed above. The parameter, c, corresponding to these contours may be computed from the axial ratio, c/a, of 1.461.

| | FOR SIGMA WITH THOSE OBSERVED | | | | | | | | |
|-----|-------------------------------|----------------------------------|----------------------------------|---------------------------------|--|--|--|--|--|
| hkl | d | Sin ² 0 (Computed) | Sin ² 0 (Observed) | Sin ² 0 (Ob Com.) | | | | | |
| 113 | 2.50vw | 0.2114 | 0.2088 | -0.0026 | | | | | |
| 122 | 2.36vw | 0.2339 | 0.2344 | + 0.0005 | | | | | |
| 004 | 2.27m | 0.2547 | 0.2533 | -0.0014 | | | | | |
| 220 | 2.22vw | 0.2722 | 0.2650 | -0.0072 | | | | | |
| 203 | 2.16vw | 0.2794 | 0.2795 | +0.0001 | | | | | |
| 221 | 2 .1 25s | 0.2881 | 0.2890 | +0.0009 | | | | | |
| 300 | 2.065m | 0.3063 | 0.3063 | 0.000 | | | | | |
| 123 | 2.034vw | 0.3135 | 0.3155 | +0.0020 | | | | | |
| 301 | 2.019m | 0.3222 | 0.3202 | -0.0020 | | | | | |
| 222 | 1.967m | 0.3359 | 0.3376 | +0.0017 | | | | | |
| 131 | 1.925s | 0.3562 | 0.3521 | -0.0041 | | | | | |
| 302 | 1.879m | 0.3700 | 0.3695 | -0.0005 | | | | | |
| 204 | 1.833w | 0.3908 | 0.3885 | -0.0023 | | | | | |
| 124 | 1.757w | 0.4249 | 0.4228 | -0.0021 | | | | | |
| 115 | 1.663vw | 0.4661 | 0.4721 | *0.0060 | | | | | |
| 133 | 1.637vw | 0.4832 | 0.4887 | +0.0055 | | | | | |
| 232 | 1.608vw | 0.5061 | 0.5050 | -0.0011 | | | | | |

TABLE III

COMPARISON OF Sin²O COMPUTED ON THE BASIS OF TETRAGONAL STRUCTURE

s = strong, m = medium, w = weak, vw = very weak.





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