3982

NACA TN 2603

TECH LIBRARY KAFB, NM
0065542

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2603

SURVEY OF PORTIONS OF THE COBALT-CHROMIUM-IRON-NICKEL QUATERNARY SYSTEM

By E. L. Kamen and Paul A. Beck

University of Notre Dame

Washington

February 1952

AFMDC
TECHNICAL LIBRARY
AFL 2811

TECH LIBRARY KAFB, NM
0065542

1V

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2603

SURVEY OF PORTIONS OF THE COBALT-CHROMIUM-IRON-NICKEL QUATERNARY SYSTEM

By E. L. Kamen and Paul A. Beck

SUMMARY

An isothermal survey was made of certain portions of the chromium-cobalt-nickel-iron quaternary system at 1200° C. The iron content was varied up to 30 percent to include the range of commercial chromium-cobalt-nickel alloys. As a part of the quaternary system, the cobalt-chromium-iron ternary system was also studied.

INTRODUCTION

A project has been initiated at the Metallurgy Department of the University of Notre Dame for the study of phase diagrams pertinent to certain alloys commercially used for high-temperature service. In a previous report (reference 1) on work done in connection with this project, an isothermal survey of the ternary chromium-cobalt-nickel system was given for 1200° C.

In order to make the results of the investigation valuable for practical applications, it was foreseen that the work would have to be extended to cover more complex systems and, in certain critical composition ranges, also to include lower temperatures. The work covered by the present report was carried out in accordance with this general plan.

Some of the most important alloy components occurring in commercial alloys of chromium-cobalt-nickel base are iron, molybdenum, silicon, and carbon. In order to proceed systematically and thoroughly in this work, it was planned to explore at first the effects of the addition of each of these elements separately. In the present work an isothermal survey of the practically most important portion of the chromium-cobalt-nickel-iron quaternary system at 1200° C was made. The iron content was varied up to 30 percent to include the range of commercial alloys of chromium-cobalt-nickel base. Since at 1200° C most of these alloys consist largely of face-centered cubic solid solutions, it was considered that the limits of solid solubility of this phase with varying iron contents would be of the most immediate concern.

In the course of this work it became evident that one of the component ternary systems, the cobalt-chromium-iron system, has not been adequately explored by previous investigators. (See literature survey.) It was, therefore, decided to divert a part of the efforts to the survey of this ternary system at 1200° C. At this temperature the sigma phase does not occur in the binary iron-chromium system. However, at temperatures below 825° C, which are of practical importance, the iron-chromium system does have a stable sigma phase. It was therefore of importance in the understanding of phase equilibriums in the cobalt-chromium-iron system to explore the relationships between the isomorphous sigma phases occurring at those temperatures in the two binary systems cobalt-chromium and iron-chromium. This work was originally started with the collaboration of Mr. W. D. Manly and briefly reported in reference 2.

In order to extend the investigation to lower temperatures, which are practically significant, some work was done on the limits of the face-centered cubic solid solutions (alpha phase) of the chromium-cobalt-nickel alloys to temperatures down to about 850° C. From the data obtained an isothermal section of this portion of the chromium-cobalt-nickel ternary system was constructed for 900° C.

In reference 1 the phases of the chromium-cobalt-nickel system were designated in accordance with the chromium-cobalt binary diagram by Elsea, Westerman, and Manning. (An exception was the sigma phase, which the above authors designated as gamma.) Following this nomenclature in the present report, alpha denotes the face-centered cubic solid solutions based on cobalt and nickel, beta refers to the hexagonal solid solutions based on cobalt, and epsilon designates the chromium-base body-centered cubic solid solutions. Since the present work concerns alloys with iron, this nomenclature leads unfortunately, but inevitably, to contradictions with the usual designations of the allotropic forms of iron.

This work was conducted at the University of Notre Dame under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

The authors wish to thank Mr. Francis Pall for doing much of the work relating to the alpha and beta phase boundaries in the cobalt-chromium-nickel system at 900° C and Mr. William D. Manly for making the initial survey of the sigma phase at 800° C in the cobalt-chromium-iron ternary system. Mr. William Kuhn of the Titanium Alloy Manufacturing Co. collaborated in the early stages of portions of the work. Mr. J. D. Nisbet of the General Electric Co. kindly contributed a series of cobalt-chromium-iron alloys. The Battelle Memorial Institute kindly made the nitrogen analysis in two cobalt-chromium-nickel alloys.

LITERATURE SURVEY

The alloy systems pertinent to the cobalt-chromium-iron-nickel quaternary phase diagram comprise the following six binary systems and four ternary systems: Cobalt-chromium, cobalt-iron, cobalt-nickel, chromium-iron, chromium-nickel, and iron-nickel, and cobalt-chromium-iron, cobalt-chromium-nickel, cobalt-iron-nickel, and chromium-iron-nickel.

All of the binary diagrams were thoroughly investigated. The cobalt-chromium system was most recently determined by Elsea, Westerman, and Manning (reference 3). The cobalt-nickel system was investigated by several workers; essentially, it features an extended range of solid solutions with a transformation at high percentages of cobalt. The most reliable data are presented in the "Metals Handbook" (reference 4, p. 1192). The latest phase diagram for the chromium-nickel system was published by Jenkins, Bucknall, Austin, and Mellor (reference 5).

The cobalt-iron system was reviewed recently by Ellis and Greiner and their diagram is given in reference 6. The chromium-iron diagram has been the subject of many investigations. It was reviewed recently by Bain and Aborn in the "Metals Handbook" (reference 4, p. 1194). The binary system of iron and nickel is presented on page 1211 of reference 4.

No high-temperature phase diagram for the cobalt-iron-nickel ternary system could be found in the literature, although some work has been done on phase equilibriums at lower temperatures and on transformations in the face-centered cubic ternary solid solutions (references 7 and 8). Portions of the chromium-iron-nickel ternary system were extensively investigated. A section representing average conditions at 900° C to 1300° C appeared in the "Metals Handbook" (reference 4, p. 1261). Rees, Burns, and Cook (reference 9) published recently their work on a portion of this ternary system, with high-purity alloys, at temperatures of 650° C to 800° C. Pugh and Nisbet (reference 10) have just published phase-diagram information relating to this system. An isothermal section which they have determined for 1100° C is in substantial agreement with the section given in reference 4. The cobalt-chromium-nickel system was investigated by Manly and Beck (reference 1) at 1200° C. Certain minor corrections were made in the course of the present work and a revised diagram appears in this report. Elsea and McBride (reference 11) investigated the effect of nickel and iron additions on the alpha-beta and beta-sigma transformations of the cobalt-chromium binary system. However, they made no claim for achieving equilibrium conditions.

The cobalt-chromium-iron alloys containing 30 percent to 90 percent iron were extensively examined by Koster (reference 12). His data were

published in the form of a series of constant iron sections. Interpolations from his data were carried out for 1200° C, and the resulting isothermal diagram, together with the results of the present investigation for the same temperature, is given in this report. Koster's paper contains a diagram of the cobalt-chromium-iron system at room temperature. This diagram does not have a phase based on the complex sigma phase in the chromium-iron system. This is in contradiction with presently accepted data for that binary system. Another point of interest, reported by Sully and Heal (reference 13), is that the sigma phase of the chromium-iron binary system is isomorphous with the intermediate phase occurring in the cobalt-chromium system. Beck and Manly (reference 2) showed that, in the cobalt-chromium-iron ternary system at 800° C, the two isomorphous binary phases are connected by a continuous series of ternary solid solutions.

EXPERIMENTAL PROCEDURE

The equipment used in this work and the procedures of melting and homogenizing were the same as those described by Manly and Beck (reference 1). The lot analyses of the cobalt rondelles, of the electrolytic chromium and nickel, and of the hydrogen-annealed electrolytic iron used for making up the alloys are given in table I. The crucibles used for melting were of alundum, zirconia, stabilized zirconia, or beryllia. Table II gives the type of crucible used for melting each alloy.

It was found that the extent of segregation in the ingots varied considerably with the alloy composition. Ingots with diameters of less than 1 inch were usually better than larger ones. Because of the lower oxide content in the bottoms of the ingots (oxide particles float to the top of the melt), the bottom portions were mainly used for examination. Samples for chemical analysis were taken from a part of the ingot directly adjacent to that used for microscopic and X-ray studies. Several chromium-cobalt-iron ternary alloys were made available by Mr. J. D. Nisbet of the General Electric Co. These were received as vacuum-melted and centrifugally cast samples and were further handled in the same way as the ingots made at Notre Dame.

All alloys used to determine the alpha phase boundaries in the quaternary system of cobalt-chromium-iron-nickel were annealed for 20 minutes at 1200° C and then forged before the final homogenizing treatment. All ternary alloys of cobalt-chromium-iron not containing appreciable amounts of the sigma or epsilon phases were also forged. None of the alloys used for determining the limits of the sigma phase at 800° C in the cobalt-chromium-iron system could be forged because of brittleness. The alloys used to establish the 900° C alpha and beta phase boundaries in the cobalt-chromium-nickel system were annealed for 20 minutes at

1200° C and then forged; after this, they were placed in the furnace for 4 additional hours at 1200° C and forged again before the homogenizing treatment at various final annealing temperatures.

The forged cobalt-chromium-iron-nickel alloys were given a homogenizing treatment of 13 hours or 75 hours at 1200° C, at the end of which time they were quenched in cold water. The forged cobalt-chromium-iron alloys were homogenized for 75 hours or more at 1200° C and quenched. The alloys which were not forged were annealed for 95 hours or more at 1200° C and quenched. The cobalt-chromium-iron alloys annealed at 800° C received 48-hour to 150-hour homogenizing treatments before quenching. The double-forged cobalt-chromium-nickel alloys were annealed for 48 hours to 180 hours at the appropriate homogenizing temperature and then quenched. The procedures described gave in most cases a good approximation of equilibrium conditions, as shown by the fact that a further increase in the annealing time produced no detectable change in the microstructure. The alloys containing considerable amounts of the sigma or epsilon phases, which were too brittle to be forged, probably did not approach equilibrium nearly so closely as the forged and double-forged alloys.

After the final homogenizing treatment the X-ray powders were taken from the specimen and microscopic samples were prepared and examined for the presence or absence of a second phase. Thus, the phase boundaries were established by the disappearing phase method.

The metallographic preparation at first used consisted of mechanical polishing with successively finer abrasives, the final stage being a Gamal polish on Buehler microcloth. A satisfactory electrolytic polishing solution was later found. The electrolytic method was rapid and it removed the surface layer of the specimen which was cold-worked by previous polishing. As a result, the number of scratches appearing after etching was greatly reduced. The conditions under which satisfactory electrolytic-polishing effect was obtained were the following:

Solution, cubic centimeters:	
Ethyl alcohol	75
Distilled water (nonexplosive)	14
Perchloric acid	6
Cathode	Stainless steel
Time, seconds	10 to 20
Current density, amperes per square inch specimen surface	10 to 12
Voltage, volts (d-c.)	6 to 10
Electrode spacing, inch	1/4
Temperature, °C	25 to 55

This method of preparation was used after a preliminary mechanical polishing on 600 abrasive paper. If kept in a covered container, the solution could be used for 1 day after being mixed.

The following etching reagents were used in addition to those described in reference 1.

(1) Etchant for the alpha phase:

Hydrochloric acid, cubic centimeters	8
Nitric acid, cubic centimeter	0.5
Glycerin, cubic centimeters	2
Cupric chloride, milligrams	50 to 150

Specimens were immersed in the etchant for several minutes or swabbed with cotton saturated with etchant for quicker action. The structure of all alpha alloys was revealed. Twins, transformation striations, and grain boundaries became apparent. The alpha phase appeared slightly amber-colored in comparison with the sigma and epsilon phases. Etching of the beta phase revealed grain boundaries. In the larger beta particles a Widmanstätten precipitate was often found. This further helped in identification. The grain boundaries in the epsilon phase were, also, revealed with this etch, but the sigma phase was unattacked. A Widmanstätten precipitate in certain epsilon alloys was attacked. The epsilon and the sigma phases had the same etching characteristics when present as small particles in an alpha matrix. This made it very difficult to determine microscopically the alpha corner of the alpha-plus-sigma-plus-epsilon three-phase field. Prolonged etching of small amounts of epsilon and sigma phases stained them light brown to dark brown.

(2) Electrolytic etchant for cobalt-chromium-iron alloys containi low percentages of iron and over 40 percent chromium:

Oxalic acid, grams	8
Distilled water, cubic centimeters	92
Cathode	Stainless steel
Time, seconds	5 to 15
Current density, milliamperes per square inch specimen surface	200
Voltage, volts (d-c.)	6
Electrode spacing, inch	1/4 to 1
Temperature, °C	25 to 35

The alpha phase appeared slightly amber-colored. The epsilon phase was etched white. Its grain boundaries and the presence of a Widmanstätten precipitate were revealed. The sigma phase remained unattacked and appeared white.

Whenever phase identification by microscopic means was doubtful X-ray diffraction was used. Powder samples were obtained from the homogenized alloys by filing or crushing in a mortar. The powders were annealed for 10 minutes at 1200° C in evacuated sealed silica tubes and quenched in cold tap water. The X-ray patterns were taken with an asymmetrical focusing camera of 20-centimeter diameter, using unfiltered chromium radiation. The usefulness of the X-ray diffraction method for phase-identification purposes was limited by its relative insensitivity in detecting small amounts of a second phase. In the case of the sigma phase this difficulty was augmented by the loss of this brittle phase in filed powders. It was necessary to crush severely rather than file specimens of two-phase alloys close to the alpha boundary in order to retain the sigma phase in the powders.

The above-mentioned difficulty in determining the alpha corner of a three-phase field could be surmounted in some cases by an X-ray diffraction method. The variation in lattice parameter of the saturated alpha alloys along the boundary was plotted as a function of the iron content for the cobalt-chromium-iron alloys annealed at 1200° C and as a function of the cobalt content in the quaternary alloys containing 10 percent iron. The three-phase corner is revealed by a more or less sharp break in the curve of lattice constant against composition, as shown previously (reference 1).

EXPERIMENTAL RESULTS

Cobalt-chromium-iron ternary system at 1200° C.- The phase diagram determined for the cobalt-chromium-iron ternary system at 1200° C is presented in figure 1 from the data in table III. (See fig. 2 also.) The table gives for each alloy the identity and the approximate amount of the various phases it contains, as estimated from the microstructure. For comparison, the amounts of the phases corresponding to alloy composition in the ternary phase diagram given in figure 1 are also indicated. The phases as identified by means of X-ray diffraction are indicated in each case where such data were available. The analyzed chemical compositions reported in table III originally contained varying amounts of an acid-insoluble material, mainly chromium oxide. These compositions were corrected to 100-percent-metal content. Several alloys of the cobalt-chromium-nickel ternary system and two alloys from the chromium-cobalt-iron ternary system were analyzed for carbon. The results are reported in table IV. The low carbon content is in accordance with the fact that no carbides were microscopically observed in any alloys.

The phase diagram is dominated by two large areas of solid solutions. The epsilon phase based on chromium has a body-centered cubic structure. The alpha phase based on the cobalt-iron solid solutions at 1200° C has

a face-centered cubic structure. The brittle solid solutions based on the complex sigma phase are found only in a limited region of the phase diagram. The maximum amount of iron soluble in this phase at 1200° C is about 18 percent.

Certain binary alloys of cobalt and iron are known to transform from the face-centered cubic structure to the body-centered cubic structure upon cooling from 1200° C to room temperature, even if the cooling is very fast. The addition of chromium does not appear to suppress this transformation. That portion of the alpha phase field labeled "A" in figure 1 designates those ternary solid solutions of cobalt, chromium, and iron which completely transform to the body-centered cubic structure (ferrite) upon quenching to room temperature. In table III, the alloys within area A are stated to contain the alpha phase, since at 1200° C that phase must have been the stable one in these alloys. The microstructure of the quenched alloys showed that the phase present at room temperature must have formed by a martensitelike reaction within the grains of the high-temperature phase originally present (see figs. 3 and 4). The X-ray patterns of these alloys consisted of two diffuse diffraction lines corresponding to the indices (110), $K\alpha_1$ and $K\beta$ chromium radiation, of the ferrite lattice. The dashed line which partially bounds area A was drawn to conform with the results of the work on binary cobalt-iron alloys by Ellis and Greiner (reference 6) and with the X-ray diffraction data obtained in the present work with alloys 1T27, 1T33, 212, and 300.

In the composition range of area B the transformation upon quenching was clearly different from that taking place in the alloys of area A. This was shown by both the microstructures and the X-ray diffraction patterns. Typical structures of alloys in area B are reproduced in figures 5 and 6. Although alloy 212 is placed in area B according to X-ray diffraction findings, its microstructure (fig. 3) corresponds to that of alloys in area A. (See fig. 7 for structure of an alloy of area B which did not transform when quenched from 1200° C to room temperature.)

The X-ray diffraction patterns of alloys which had alpha phases corresponding to compositions in area B contained lines of the alpha phase, along with some unidentified extra lines. These extra lines, not reported in table III, are tabulated in table V. No specific investigation was undertaken to examine the nature of the transformation taking place upon cooling in area B, since it would have curtailed the work being done to determine phase boundaries at 1200° C.

Chromium-rich alloys in the epsilon phase field were found to have a Widmanstätten type of precipitate similar to that previously found in chromium-rich alloys in the epsilon phase field of the cobalt-chromium-nickel ternary system. This precipitate was observed in alloys as low in chromium as 309 (nominal composition, cobalt - 26.75 percent,

chromium - 42.25 percent, and iron - 31 percent). Manly and Beck (reference 1) have described how this precipitate was identified as sigma phase, probably formed during cooling. Similar conclusions were reached in the present work with regard to the precipitate in this alloy system. It was also pointed out (reference 1) that the sigma precipitate did not extend to the grain boundaries of the epsilon matrix. The same phenomenon was found in the cobalt-chromium-iron system. It was also observed that the precipitate is not revealed near the boundaries of second-phase particles in an epsilon matrix by the etching method used (figs. 8 and 9). In the epsilon phase of alloy 277, which contained particles of epsilon phase with precipitate, in a sigma-phase matrix, a layer of differing etching characteristics was observed in that part of the epsilon phase directly adjacent to the sigma phase and not containing precipitate particles. A photomicrograph of this structure is shown in figure 10. Some of the cracks which occur in the sigma phase did not penetrate this layer, while other cracks penetrated through the intermediate layer, up to but not into that portion of the epsilon phase containing the precipitate. Quite likely, this intermediate layer may be a phase different from both epsilon and sigma. Manly and Beck (reference 1) found that the sigma precipitate formed very large plates in an alloy (18T36) melted at the General Electric Co., Schenectady laboratory, in contrast with the finer platelets of the precipitate found in alloys of similar composition (e.g., alloy 19) melted at Notre Dame. Analysis for nitrogen in alloys 19 and 18T36, kindly carried out at Battelle Memorial Institute, gave 0.005 to 0.007 percent and 0.263 percent, respectively. These results indicate that nitrogen may stimulate the growth of the sigma precipitate particles during cooling from elevated temperatures. The structure of the epsilon phase alloys with high iron content which did not contain a precipitate is shown in figure 11. Apart from impurity phases, this is a typical structure for a single-phase solid solution not containing annealing twins.

The brittle sigma phase occurs in a relatively small region of the cobalt-chromium-iron system at 1200° C. Since the sigma phase is not stable in the chromium-iron binary system at 1200° C, it does not extend through the ternary system at that temperature. Typical structures of the brittle sigma phase (with cracks) coexisting with alpha and epsilon phases are presented in figures 9, 12, and 13.

The two-phase region existing between the epsilon and sigma phases becomes very narrow as iron is added to the cobalt-chromium binary alloys. Increasing iron content has the same effect on the alpha-epsilon two-phase region. However, this two-phase field becomes narrow over a wider range of increasing iron contents. The alpha and sigma phase boundaries of the alpha-plus-sigma two-phase field run approximately parallel to one another. The three-phase field is extremely narrow. This is a result of the very narrow two-phase epsilon-plus-sigma field.

Segregation difficulties were most severe in alloys with compositions along the epsilon phase boundary in the vicinity of the epsilon and sigma corners of the three-phase field. The segregation was frequently found in the form of a "clotlike" microconstituent, apparently sigma phase, containing a fine, possibly eutectic, dispersion of another phase. A typical structure is presented in figure 14. The extremely small platelets of the second phase were not coalesced by an annealing period of 480 hours at 1200° C. The etching characteristics of this phase with respect to the sigma matrix corresponded to the etching characteristics of epsilon particles in a sigma matrix. The tentative identification of the precipitate as epsilon phase is in accord with its occurrence in alloys 367 and 368 (fig. 15) which are located in the three-phase field and in alloys 282 and 346 of the epsilon-plus-sigma two-phase field. The X-ray diffraction patterns of alloys 367 and 368 contained lines of the alpha phase and epsilon phase. The only microconstituent to which the epsilon phase lines can be ascribed is the finely distributed phase. The question marks in the epsilon column of table III refer to this tentatively identified finely dispersed phase.

Severe segregation was noted in 22 alloys marked in table III as "Segregated." The microstructure showed great variation of phases present from bottom to top of these ingots. They were neglected when the phase boundaries in figure 1 were placed. Apart from such difficulties, which were mainly encountered near the tip of the sigma phase, it was possible to establish the boundaries of the single-phase fields by observing the disappearance of a second phase.

By fitting together the microscopic evidence available from a number of alloys, the corners of the three-phase field have been placed at the following points:

Corner	Percent Co	Percent Cr	Percent Fe
Alpha	42.75	32.25	25
Epsilon	31.75	48.25	20
Sigma	32.25	49.75	18

It was difficult to estimate the amounts of second phases present in a finely distributed form. This was especially true for the fine distribution of second phase which is probably epsilon phase in a eutectic distribution.

The following discrepancies were encountered in regard to the phase boundaries in figure 1. Alloys 191, 192, and 300 each had traces of second phase in an alpha matrix but were placed just within the alpha field. Alloy 373 (fig. 12) was placed just within the three-phase field,

although microscopic observation gave evidence of only alpha and sigma phases in the microstructure. Alloy 108 was placed in the two-phase alpha-epsilon field in accordance with its chemical analysis, although its structure was entirely epsilon phase. Its composition as calculated from the amounts of the components used in melting would place this alloy in the epsilon phase field in accordance with the microstructure. Alloy 363 was placed just within the sigma phase field but had a fine dispersion of second phase, probably epsilon. These minor discrepancies are almost negligible in view of the consistency of the large amount of other data, but they do indicate that some caution must be observed in estimating the accuracy of the results. Some inconsistencies were observed between the microstructure and the X-ray diffraction results, such as the presence of lines of the alpha phase in X-ray diffraction patterns of several alloys in the epsilon phase field, the microstructures of which did not show alpha phase. The presence of sigma phase lines in diffraction patterns in epsilon phase alloys is readily explained by the presence of the sigma precipitate in the epsilon phase. In several cases in the X-ray patterns of two-phase alloys, which contained the brittle sigma phase, the lines of the sigma phase were missing. The manner in which the epsilon phase was lost in X-ray diffraction patterns cannot be accounted for. Similar observations were made previously in the chromium-cobalt-nickel system (reference 1). However, for all alloys showing such discrepancies, the internal consistency of the microscopic observations was quite satisfactory and the phase boundaries were located in accordance with those results.

Boundaries of sigma phase at 800° C in cobalt-chromium-iron system.- The limits of the sigma phase at 800° C are plotted in figure 16 from the data in table VI. (Also see fig. 17.) These boundaries have been drawn with dashed lines since the alloys could not be forged and the annealing periods used may not have been long enough to insure equilibrium conditions. In reference 2 Beck and Manly stated that the sigma phase in the cobalt-chromium-iron system was a series of solid solutions at 800° C. Careful microscopic examination with several etching reagents was unable to detect two sigma phases in any part of the sigma field. Additional data obtained in the present work with new alloys gave the same result. The sigma phase did not exhibit any structure. The microscopic results were in good agreement with each other, even though a variety of homogenizing periods were used. Many of the alloys used for this work were also examined after homogenizing at 1200° C. Comparison of the microstructures showed that many alloys which did not entirely consist of sigma phase or which did not contain any sigma phase at 1200° C consisted mostly or entirely of sigma phase at 800° C.

Alpha phase and beta phase boundaries in cobalt-chromium-nickel system at 900° C.- The alpha phase and beta phase boundaries are plotted in figure 18 from the data in table VII. (See also fig. 19.) The alpha boundary at 1200° C from reference 1 has been included in the plot for

purposes of comparison. Alpha has a face-centered cubic structure and beta has a hexagonal close-packed structure.

An initial survey of the change in the extent of the alpha phase field with decreasing temperature was made with five alloys with compositions of a few percent less chromium than corresponds to the alpha phase at 1200° C. These alloys were double-forged (see section "Experimental Procedure") and annealed at various temperatures as indicated in table VIII. These alloys were examined for the presence of a second phase. The temperature at which a second phase began to precipitate was bracketed by two temperatures: The lowest temperature at which second phase was not found and the highest temperature at which second phase was observed. The location of the boundary at 900° C could be estimated from this information and alloys were then made to determine the boundary at that temperature. The precipitation of a second phase at one temperature, but not at a higher temperature for similar annealing periods with the same alloy, lends support to the belief that the 900° C alpha phase boundary in figure 18 represents conditions close to equilibrium.

The alloys prepared for the final determination of the alpha and beta boundaries at 900° C were also double-forged and quenched after final anneal at 900° C. The data used for these boundaries were in good agreement, except for alloy 237, which was placed just inside the two-phase field, although it did not show second phase in microscopic examination. The three-phase-field corner at the beta phase has been placed at a composition of cobalt - 64 percent, chromium - 33 percent, and nickel - 3 percent. The alpha corner of the three-phase field (alpha plus beta plus probably sigma) has been placed at a composition of cobalt - 63 percent, chromium - 33 percent, and nickel - 4 percent. The etching characteristics of the second phase in equilibrium with the alpha matrix changed distinctly between alloys 333 and 334. This change may well correspond to the alpha corner of the assumed three-phase field: Alpha plus epsilon plus sigma.

A transformation occurring in alpha alloys of the cobalt-chromium system was found in alpha boundary alloys containing up to about 24 percent nickel. A typical structure resulting from this transformation is presented in figure 20. The alpha-plus-beta two-phase region is very narrow with respect to composition in the ternary system and it is probably also limited with respect to temperature, as indicated by the data on the binary cobalt-chromium system (reference 3).

The Widmanstätten precipitate observed in certain beta alloys could not be positively identified by X-ray diffraction probably because of the small amount present in any specimen. However, this precipitate did have the same etching characteristics with respect to the beta matrix as had massive particles of sigma with respect to a beta matrix.

The binary cobalt-chromium diagram (reference 3) indicates decreasing solubility of the sigma phase in the beta phase with decreasing temperature. For these two reasons, it is believed that the Widmanstätten precipitate observed consisted of the sigma phase. Figure 21 is a photomicrograph of an alloy with a beta matrix containing the Widmanstätten precipitate. The precipitate was often missing in small grains of beta. Figure 22 shows the structure of an alloy containing transformed alpha phase and some beta grains without precipitate. In all alloys in which alpha and beta coexist at the annealing temperature, after quenching the alpha phase was striated, as shown in figure 22. It is believed that this striation is a result of a transformation occurring in the alpha phase upon cooling to room temperature. As a result of the transformation in the alpha phase, small amounts of beta could easily be detected in etched specimens. Figure 23 illustrates the presence of a small amount of second phase, other than beta, in alloys which were used to determine the boundary. The specimen was not etched before taking the photomicrograph in order to prevent the removal by the etching reagent of the smallest second-phase particles.

Alpha phase boundaries in cobalt-chromium-iron-nickel system at 1200° C.- The isothermal section of a quaternary alloy phase diagram would be represented by a tetrahedron. This method of representation is not very convenient, since a three-dimensional model is not easily constructed or reproduced. However, it is possible to plot the phase boundaries in such a system on a two-dimensional scale. This is done by keeping the amount of one of the components constant and varying the ratio of the other three elements. The data may be plotted on an equilateral triangle, corresponding to a section of the tetrahedron parallel to one of its boundary planes. By changing the amount of the element which is being kept constant, a series of two-dimensional triangular sections can be plotted for the other three components, one section for each constant composition of the first component. As the amount of the first component increases, the size of the triangular sections of the tetrahedron becomes smaller. In order to offset the decreasing size of the triangular map and at the same time to plot and compare directly the data for several constant amounts of the first component in the same two-dimensional figure, the amounts of the three varying components may be increased to a total of 100 percent, disregarding the constant amount of the first component. The calculation is done by dividing the actual percentage of a component by the fraction of the sum total of the percentages of all three varying components in the alloy.

In the present study, constant compositions of 10, 20, and 30 percent iron in combination with variable amounts of cobalt, chromium, and nickel were used. The correction factors were, respectively, 10/9, 10/8, and 10/7. The analyses of iron in the alloys were not exactly 10, 20, or 30 percent. However, the composition of the other components in the

alloys were corrected on the basis of 10-, 20-, or 30-percent-iron contents. In this manner figure 24 shows data for constant amounts of 10, 20, and 30 percent iron, giving the ratios of cobalt, chromium, and nickel corresponding to the alpha phase boundary. The composition of each alloy and of the phases occurring in it is given in table IX for all alloys used in plotting the boundaries in figure 24. (Also see fig. 25.) The alpha phase boundary for alloys with no iron from the report (reference 1) by Manly and Beck is included in the plot for comparison. The actual maximum solubility of chromium in the alpha phase is replotted in figure 26 as a function of the actual cobalt content for alloys containing 0, 10, 20, and 30 percent iron. These data were interpolated from the phase boundaries in figure 24. The data are in table X.

The data for each of the three boundaries were in good agreement. The alpha phase coexists with the epsilon phase and the sigma phase in alloys containing 0, 10, and 20 percent iron. The corner of the three-phase field alpha plus epsilon plus sigma was determined only for alloys containing 10 percent iron. It could not be done metallographically, because no etchant was found which would distinguish between epsilon and sigma in these alloys. X-ray diffraction patterns were made for alloys containing sufficiently large amounts of the additional phases. Diffraction patterns for alloys 200, 214, and 193 roughly bracketed the three-phase-field corner. The diffraction pattern for alloy 200 had alpha-plus-sigma phases, that for alloy 214 had alpha-plus-epsilon-plus-sigma phases, and that for alloy 193 had alpha-plus-epsilon phases. Measurements were made of the lattice parameter of the alpha phase from diffraction patterns made of a series of boundary alloys. For each pattern the lattice parameter of the alpha phase was calculated from the three highest-angle alpha phase lines. The parameter was plotted against the $\cos^2\theta$ value for these three diffraction lines for each alloy. The plot was extrapolated to $\cos^2\theta$ equal to 0, and the corresponding value of the lattice parameter was used. This value of lattice parameter was plotted in figure 27 as a function of the corrected cobalt composition of the alpha phase in alloys containing 10 percent iron. The data are in table XI. No explanation can be given for the discrepancy in alloy 207. This procedure locates the corner of the three-phase field at an actual composition of cobalt - 30.6 percent, chromium - 38.7 percent, iron - 10 percent, and nickel - 20.7 percent, which is consistent with the results obtained by phase identification as described above.

The three-phase-field corner at the alpha phase in the 20-percent-iron section was not determined accurately. However, from the data of the cobalt-chromium-iron system and from the X-ray diffraction pattern of alloy 149, which showed alpha, epsilon, and sigma lines, it is possible to estimate that this corner lies between actual nickel contents of 2 to 6 percent. The alloys containing 30 percent iron did not have sigma phase at 1200° C, and alloys 248, 252, and 199 were found to contain, by X-ray

diffraction methods, alpha and epsilon phases. Typical structures of these alloys are presented in figures 28 and 29.

A transformation in the alpha phase was observed microscopically in boundary alloys with all iron contents. Typical microstructures resulting from this transformation are very similar in appearance to those shown in figures 5 and 6. As shown by the microstructure, nickel between 17 percent and 27 percent suppressed the transformation in boundary alloys with no iron. Between 13 percent and 18 percent nickel suppressed the transformation in boundary alloys with 10 percent iron. Between 8 percent and 13 percent nickel suppressed the transformation in boundary alloys with 20 percent and 30 percent iron.

In the X-ray diffraction patterns of several quaternary alloys containing the alpha phase, a set of unidentified diffraction lines was observed. Since these lines were always observed to appear together, they were ascribed to an unknown "Z" phase. This set of diffraction lines is listed with the values of θ in table XII. The structure corresponding to these lines does not appear to be a simple face-centered or body-centered cubic, or a hexagonal close-packed crystal structure.

The Z phase lines were found together with alpha phase lines in diffraction patterns of filed and annealed X-ray specimens of alloys 133, 150, 194, 199, and 200. All of these alloys contained 10 percent iron, except 199, which had 30 percent iron. Alpha and Z phase lines were also found in X-ray diffraction patterns of filed and annealed X-ray specimens of two alloys with the same cobalt-chromium-nickel ratio as alloy 133, but containing $3\frac{1}{2}$ and 7 percent iron, respectively. When an X-ray specimen from alloy 133 was prepared by crushing the annealed alloy in a mortar, the diffraction pattern, after annealing and quenching of the powder, showed alpha-plus-sigma phases but no Z lines. The same result was obtained when crushed powders of alloy 133 were quenched from 1200° C to temperatures of 250° C and 100° C.

No detailed investigation of the occurrence of the Z phase was undertaken, but the following statements concerning it can be made:

(1) Z diffraction lines were always found together with the diffraction lines of the alpha phase.

(2) Z phase was found only in diffraction patterns of filed X-ray specimens but not of crushed powders.

(3) Z diffraction lines were also found in two X-ray diffraction patterns of alloys which did not show transformation striations in the microstructure of the alpha phase. These two alloys, 194 and 199, had an alpha matrix microscopically similar to that of the alpha phase in figures 28 and 29.

DISCUSSION OF RESULTS

The technologically most important portion of the cobalt-chromium-nickel-iron phase diagrams is the face-centered cubic alpha phase region. The alpha phase field in the cobalt-chromium binary system is quite broad at 1200° C. In ternary cobalt-chromium-iron alloys, the alpha phase field forms a continuous series of solid solutions between the cobalt-chromium and the chromium-iron binary systems, adjoining to the face-centered cubic phase of the cobalt-iron binary system uninterrupted at 1200° C. The maximum solubility of 34 percent chromium in the alpha phase of cobalt-chromium alloys at 1200° C is decreased in the ternary cobalt-chromium-iron system with increasing iron content to the lower solubility of chromium in the binary chromium-iron system. The maximum solubility of chromium in the alpha phase of this binary system is 11 percent at 1200° C. The value of 11 percent chromium for this solubility found in the present work exceeds the value of 9 percent previously reported (reference 4, p. 1211) by an amount which is unlikely to be experimental error.

The limit of the alpha phase at 1200° C in the cobalt-chromium system was found to be in good agreement with the work of Manly and Beck (reference 1) and with other previous investigations. Koster has published a paper (reference 12) relating to phase equilibriums in the cobalt-chromium-iron ternary system. Isothermal data for 1200° C were obtained from Koster's results, by interpolation, and they are plotted in figure 30 together with the corresponding results of the present investigation. The data taken from Koster's paper are presented in table XIII. The points according to Koster's results do not fall on smooth curves nor are they all in close agreement with the present work. The dashed curves in figure 30 were drawn as deemed best to fit the points obtained by interpolation from Koster's data.

Manly and Beck (reference 1) have shown that the alpha phase field is very broad at 1200° C in ternary cobalt-chromium-nickel alloys. In the present investigation the extension of the alpha phase in quaternary alloys of cobalt-chromium-iron-nickel was determined for alloys containing 10, 20, and 30 percent iron. It was found that the cobalt-chromium-nickel ratios of the alpha phase boundary alloys remained nearly the same as the iron content increased from 0 to 30 percent (fig. 24). However, the maximum solubility of chromium in the quaternary alpha phase decreased as the iron content increased (fig. 26). This plot also shows that the maximum chromium solubility in the alpha phase decreases with increasing cobalt content for any content of iron between 0 and 30 percent. Considering the practical importance of phase relationships in these alloys at temperatures lower than 1200° C, the extent of the alpha phase field in ternary cobalt-chromium-nickel alloys was determined at 900° C. At

this temperature the extent of the alpha field is a few percent chromium less than at 1200° C. The beta phase which is stable at 900° C in the cobalt-chromium system extends somewhat into the ternary cobalt-chromium-nickel system up to a nickel content of 3 percent.

The limit of the alpha phase at 900° C in the chromium-nickel system was taken from the work published in reference 5. The limits of the beta phase in the cobalt-chromium system at 900° C were placed in accordance with Elsea, Westerman, and Manning (reference 3). However, the limit of the alpha phase in the cobalt-chromium binary system at 900° C was found to be near 32.5 percent chromium, instead of 34 percent chromium as indicated by Elsea, Westerman, and Manning (reference 3).

The accuracy for the alpha phase boundaries is estimated to ±1.5 percent chromium for the cobalt-chromium-iron and cobalt-chromium-nickel ternary systems and to about ±1.5 percent chromium and ±1.5 percent iron for the cobalt-chromium-iron-nickel quaternary system. The accuracy of the three-phase-field corners is estimated to ±2 percent iron in cobalt-chromium-iron alloys and to ±2 percent cobalt in quaternary cobalt-chromium-iron-nickel alloys.

The epsilon phase extends up to about 75 percent iron in the binary alloys of chromium and iron at 1200° C and up to 25 percent cobalt in the cobalt-chromium binary alloys at 1200° C. In ternary cobalt-chromium-iron alloys the epsilon phase extends over a large portion of the system at 1200° C. However, the low-iron and low-nickel alloys in the epsilon field of the cobalt-chromium-iron and cobalt-chromium-nickel ternary systems, respectively, always contain a Widmanstätten type precipitate of the sigma phase after quenching from 1200° C to room temperature. These alloys are too brittle to be hot-forged. Ternary cobalt-chromium-iron alloys along the epsilon phase boundary, containing more than 50 percent iron, do not show sigma precipitate and were successfully hot-forged in order to approach equilibrium conditions during subsequent homogenization

The limit of the epsilon phase at 1200° C in binary cobalt-chromium alloys was taken from reference 1. The limit of the epsilon phase in binary chromium-iron alloys is 10.5 percent chromium, according to reference 4, page 1194. This value was confirmed in the present work.

At 1200° C the sigma phase exists in the cobalt-chromium system but not in the chromium-iron system. Correspondingly, in ternary alloys of cobalt-chromium-iron at 1200° C, the sigma phase forms an elongated field extending into the ternary system from the cobalt-chromium side but terminating before reaching the iron-chromium binary system.

In the ternary cobalt-chromium-iron system at 1200° C, the maximum solubility of iron in the sigma phase is 18 percent. The sigma phase

field in the ternary cobalt-chromium-iron system at 1200° C is not appreciably wider than the sigma phase field at 1200° C in binary cobalt-chromium alloys.

At 800° C the sigma phase is present in both the cobalt-chromium and chromium-iron binary systems. In the ternary cobalt-chromium-iron system at 800° C the sigma phase extends continuously from the cobalt-chromium side to the chromium-iron side as a series of solid solutions. The continuity of the sigma solid solution at 800° C was established microscopically. Alloys in the whole range were subjected to careful microscopic examination, using a variety of different etching reagents. It was impossible to detect the presence of two different sigma phases in any of these alloys. The more positive X-ray diffraction method, which is normally used in such investigations, could not be applied in the present case, since the lattice constants of the sigma phase did not vary noticeably with the iron content. This sigma phase field is much wider in ternary alloys than in either one of the adjoining binary systems. The sigma phase field in ternary cobalt-chromium-iron alloys at 1200° C lies entirely within the boundaries of the sigma phase field at 800° C (fig. 16).

Both limits of the sigma phase field in the binary cobalt-chromium system were found in the present work to occur at higher chromium contents (56 and 60 percent chromium) than previously reported (reference 3) (52 and 58 percent chromium). The midpoint between the newly established limits (56 and 60 percent chromium) corresponds closely to the cobalt-chromium atomic ratio Co_2Cr_3. The new values were found in the present work at both 800° C and 1200° C. The data obtained for ternary cobalt-chromium-iron alloys extrapolate smoothly to the revised phase boundaries of the binary cobalt-chromium system. This change in the limits of the sigma phase in binary cobalt-chromium alloys at 1200° C necessitates a corresponding slight revision of the 1200° C isothermal section of the cobalt-chromium-nickel system previously reported (reference 1). The revised cobalt-chromium-nickel phase diagram is presented in figure 31.

The X-ray diffraction patterns of cobalt-chromium-iron and cobalt-chromium-iron-nickel alloys quenched from the alpha phase field at 1200° C to room temperature showed other diffraction lines in addition to, or in place of, the lines corresponding to the face-centered cubic alpha structure. Martensitic-type transformations upon cooling from the alpha phase field at elevated temperatures are known to occur in portions of the cobalt-chromium (reference 3), cobalt-iron (reference 6), and chromium-iron (reference 4, p. 1194) binary systems.

The X-ray patterns of cobalt-chromium-iron alloys in area A (fig. 1) quenched from 1200° C to room temperatures contained only two diffuse

diffraction lines which correspond to the $[\bar{1}10]_{K\alpha_I}$ and $[\bar{1}10]_{K\beta}$ lines of a body-centered cubic lattice. The lines corresponding to the alpha phase were missing altogether. This may be interpreted as an indication of complete transformation of the alpha phase to ferrite upon cooling from 1200° C. This interpretation is supported by the martensitic microstructures (figs. 3 and 4) observed in these alloys. Furthermore, such transformations are known to occur in those portions of the cobalt-iron (reference 6) and chromium-iron (reference 4, p. 1194) binary systems which partially bound area A. It is typical of this transformation that it cannot be suppressed by fast cooling.

The diffraction patterns of cobalt-chromium-iron alloys in area B (fig. 1) contained alpha phase diffraction lines together with other diffraction lines which were not positively identified. The θ values for diffraction lines other than those of the alpha phase for alloys in area B are listed in table V.

Several X-ray diffraction patterns of quaternary cobalt-chromium-iron-nickel alloys, quenched from 1200° C to room temperature, also contained a set of extraneous diffraction lines, in addition to those belonging to the alpha phase. This set of extraneous lines, which were often observed to occur together, has been tentatively designated as belonging to an unidentified Z phase. A set of θ values corresponding to the Z phase diffraction lines is presented in table XII.

A comparison of the θ values of diffraction lines listed for the Z phase in table XII and the θ values in table V for diffraction lines of cobalt-chromium-iron alloys in area B indicates that certain lines of each correspond. However, there are θ values in table V which do not correspond to θ values for the Z phase. It is evident from the X-ray diffraction data that the alloys in this composition range partially transform upon quenching to room temperature. However, most of the alpha phase, stable at 1200° C, is retained upon quenching.

The typical microstructure of cobalt-chromium-iron alloys in area B quenched from 1200° C to room temperature is conspicuous for the straight lines, or striations, observed within each alpha grain, as shown in figures 5 and 6.

The Z phase diffraction lines were only found in X-ray diffraction patterns also containing alpha phase diffraction lines. In most cases the corresponding microstructures showed striations. However, the Z phase diffraction lines were also found in diffraction patterns of some alloys which did not have striations in the alpha phase. Tables V and XII show that the X-ray diffraction patterns of alloys in area B exhibiting striated microstructures contain diffraction lines other than those corresponding to the alpha phase or the Z phase. It may be concluded

that in cobalt-chromium-iron alloys of area B the striated microstructure corresponds to the appearance of a new phase (probably martensitic). This view is supported by microscopic observation at high magnification, which also indicates that there may be a second phase present in the lamellae of the striations (figs. 32 and 33).

Barrett (reference 14) recently published a paper dealing with crystal-structure imperfections (faults) in face-centered cubic copper-silicon alloys. Photomicrographs in Barrett's paper (figs. 10c and 10d) closely resemble the structures found in cobalt-chromium-iron alpha alloys of area B, figure 1. Barrett states on page 131 of reference 14 that the lines are similar in appearance to the bands in the banded alpha-plus-kappa structure and to thin deformation twins and that they lie on the close-packed $[\bar{1}1\bar{1}]$ planes of the face-centered cubic solid solution. He adds that because of this and the fact that they can be produced by deformation it is safe to conclude that they represent a modification of the normal stacking of matrix planes, for this would be true if they were either clusters of faults, lamellae of kappa, transition precipitate, twins, or locally distorted metal along slip planes; since the number per grain is orders of magnitude smaller than the number of faults necessary to cause the streaks that are seen in diffraction patterns it is clear that they are not individual faults. It is quite possible that the striated microstructures found by Barrett in the copper-silicon alloys, like the very similar ones found in the present work, result from a martensitic transformation, even though in the copper-silicon alloys they are not produced by quenching but only occur after plastic deformation. The transformation in ternary cobalt-chromium-iron alloys described above appears to be very similar to that observed by Elsea, Westerman, and Manning (reference 3) in the alpha phase in cobalt-chromium binary alloys after quenching. The transformation was also found to occur in certain ternary cobalt-chromium-nickel alpha phase alloys quenched from 1200° C and 900° C to room temperature. However, the transformation was suppressed in ternary cobalt-chromium-nickel alpha phase boundary alloys quenched from 1200° C when the nickel content increased to a value between 17 percent and 27 percent. The transformation in cobalt-chromium-nickel alpha phase boundary alloys quenched from 900° C was suppressed by about 24 percent nickel.

The transformation was detected in alpha phase quaternary alloys of cobalt-chromium-iron-nickel after quenching from 1200° C. In these alloys, also, nickel suppressed the transformation. In alpha phase boundary alloys containing 10 percent iron, the transformation is suppressed by a nickel content of 13 percent to 18 percent. In quaternary alloys containing 20 percent or 30 percent iron the transformation is suppressed if the nickel content is raised to 8 percent to 13 percent.

CONCLUSIONS

From a survey of a portion of the chromium-cobalt-nickel-iron quaternary system at 1200° C the following conclusions may be drawn:

1. The 1200° C isothermal section of the chromium-cobalt-iron ternary phase diagram was determined, using 154 vacuum-melted alloys. It was found to comprise an extended range of face-centered cubic (alpha) solid solutions based on the cobalt-iron binary system, of another extended range of body-centered cubic (epsilon) solid solutions based on chromium-iron solid solutions with more than 12 percent chromium. The chromium-cobalt sigma phase extends into the ternary system taking up to a maximum of 18 percent iron in solid solution. The three solid solutions coexist with each other in three two-phase fields and a narrow three-phase field. The alpha phase almost in its whole field partially or wholly transforms upon cooling from 1200° C to room temperature. This transformation cannot be suppressed by quenching; it is presumably of a martensitic nature.

2. The isomorphous cobalt-chromium and iron-chromium sigma phases were found to form a continuous series of solid solutions with each other at 800° C. This ternary sigma solid solution field is wider at 800° C than at 1200° C; the sigma field at 1200° C lies wholly within the composition range of the sigma field at 800° C.

3. Investigation of the ternary cobalt-chromium-nickel alloys at 900° C indicated that at this temperature the alpha solid solution has a somewhat smaller extension than at 1200° C. At 900° C the chromium-cobalt beta phase extends into the ternary system and takes up to a maximum of 3 percent nickel into solid solution. A martensitic transformation not suppressible by quenching, similar in microstructure to that described for the chromium-cobalt-iron alloys, was found to occur in binary cobalt-chromium alpha alloys and in ternary cobalt-chromium-nickel alpha alloys with up to about 24 percent nickel. At nickel contents higher than about 24 percent, this transformation is suppressed.

4. The extent of the alpha solid solution field at 1200° C in the chromium-cobalt-nickel-iron quaternary system was investigated at 10-, 20-, and 30-percent-iron contents. It was found that with increasing iron content, the solubility of chromium in the alpha phase decreases but that the chromium-cobalt-nickel ratios remain nearly the same. The martensitic transformation found in ternary chromium-cobalt-iron alloys was also found in quaternary cobalt-chromium-iron-nickel alpha phase boundary alloys. As the iron content in the alpha boundary alloys of the quaternary system was increased, the nickel content necessary to suppress the transformation decreased. The transformation in quaternary alloys with 10 percent iron was suppressed by 13 percent to 18 percent nickel

and in alloys with 20 percent and 30 percent iron, the transformation was suppressed by between 8 percent and 13 percent nickel.

University of Notre Dame
Notre Dame, Ind., January 31, 1950

REFERENCES

1. Manly, W. D., and Beck, Paul A.: Survey of the Chromium-Cobalt-Nickel Phase Diagram at 1200° C. NACA TN 2602, 1952.

2. Beck, P. A., and Manly, W. D.: Sigma Phase in Ternary Cr-Co-Fe and Cr-Co-Ni Alloys. Trans. Am. Inst. Min. and Met. Eng., vol. 185, 1949, p. 354.

3. Elsea, A. R., Westerman, A. B., and Manning, G. K.: The Cobalt-Chromium Binary System. Trans. Am. Inst. Min. and Met. Eng., vol. 180, 1949, pp. 579-602.

4. Lyman, Taylor, ed.: Metals Handbook. Am. Soc. Metals (Cleveland), 1948.

5. Jenkins, C. H. M., Bucknall, E. H., Austin, C. R., and Mellor, G. A.: Some Alloys for Use at High Temperatures. Part IV. Jour. Iron and Steel Inst., vol. 136, 1937, pp. 187-220.

6. Ellis, W. C., and Greiner, E. S.: Equilibrium Relations in the Solid State of the Iron-Cobalt System. Trans. Am. Soc. Metals, vol. 29, 1941, pp. 415-431.

7. Bradley, A. J., and Goldschmidt, H. J.: An X-Ray Investigation of Iron-Nickel-Chromium Alloys. Jour. Iron and Steel Inst., vol. 144, 1941, pp. 273-283.

8. Wyman, L. L.: Low-Temperature Transformation in Iron-Nickel-Cobalt Alloys. Trans. Am. Inst. Min. and Met. Eng., vol. 135, 1939, pp. 542-555.

9. Rees, W. P., Burns, B. D., and Cook, A. J.: Constitution of Iron-Nickel-Chromium Alloys at 650° to 800° C. Jour. Iron and Steel Inst., vol. 162, pt. 3, July 1949, pp. 325-336.

10. Pugh, J. W., and Nisbet, J. D.: Study of Iron-Chromium-Nickel Ternary System. Trans. Am. Inst. Min. and Met. Eng., vol. 188, 1950, pp. 268-276.

11. Elsea, A. R., and McBride, C. C.: Cobalt-Chromium Alloys. Trans. Am. Inst. Min. and Met. Eng., vol. 188, 1950, pp. 154-161.

12. Koster, W.: Das System Eisen-Kobalt-Chrom. Archiv Eisenhüttenwesen, Bd. 6, Heft 3, 1932, pp. 113-116.

13. Sully, A. H., and Heal, T. J.: An Electron Compound in Alloys of the Transition Metals. Research, vol. 1, no. 3, March 1948, p. 288.

14. Barrett, C.: Faults in the Structure of Copper-Silicon Alloys. Trans. Am. Inst. Min. and Met. Eng., vol. 188, no. 1, Jan. 1950, pp. 123-135.

TABLE I

LOT ANALYSES BY WEIGHT PERCENT

Element or compound	Cobalt rondelles	Electrolytic -		
		Chromium	Iron (H_2 anneal)	Nickel
C	0.17	0.01	0.010	----------
CaO	.12	-----	-----	----------
Co	Bal.	-----	-----	0.6 to 0.8
Cr	-----	Bal.	<.015	----------
Cu	.02	Trace	<.03	0.01
Fe	.12	.06	Bal.	.01
H_2	-----	.045	-----	----------
MgO	.04	-----	-----	----------
Mn	.06	-----	<.01	----------
Mo	-----	-----	<.015	----------
N_2	-----	.010	-----	----------
Ni	.46	-----	<.03	Bal.
O_2	-----	.51	-----	----------
P	-----	-----	.003	----------
Pb	-----	.001	-----	----------
S	.009	.012	.002	.001
Si	-----	-----	-----	----------
SiO_2	.13	-----	<.03	----------

NACA

TABLE II

CRUCIBLES USED FOR MELTING

Alloy	Crucible
101 to 153	Zirconia
154 to 156	Alundum
157 to 164	Beryllia
165 to 263	Alundum
264, 266	Zirconia
265, 267 to 269	Alundum
270 to 281	Zirconia
282 to 288	Stabilized zirconia
290 to 302, 319	Alundum
303 to 318	Zirconia
324 to 363	Stabilized zirconia
364 to 374	Alundum

TABLE III

DATA USED TO DETERMINE PHASE DIAGRAM FOR COBALT-CHROMIUM-IRON

SYSTEM AT 1200° C

Alloy	Weight percent			Phases from figure 1 (percent)			Phases found from - (percent)				Annealing time after forging (hr)
							Microstructure			X-ray	
	Fe	Co	Cr	Alpha	Epsilon	Sigma	Alpha	Epsilon	Sigma		
Alpha alloys											
1T1	9.64	81.38	8.98	100	-------	-----	100	-------	-----	Alpha	80
1T2	9.76	72.07	18.17	100	-------	-----	100	-------	-----	Alpha	80
1T3	9.87	62.54	27.59	100	-------	-----	100	-------	-----	Alpha	80
1T13	19.86	52.40	27.74	100	-------	-----	100	-------	-----	Alpha	80
1T14	19.62	62.11	18.27	100	-------	-----	100	-------	-----	Alpha	80
1T15	19.38	71.59	9.03	100	-------	-----	100	-------	-----	Alpha	80
1T16	28.96	62.40	7.59	100	-------	-----	100	-------	-----	Alpha	80
1T17	29.58	52.05	18.37	100	-------	-----	100	-------	-----	Alpha	80
1T18	29.95	42.15	27.90	100	-------	-----	100	-------	-----	Alpha	80
1T25	39.66	41.87	18.47	100	-------	-----	100	-------	-----	Alpha	80
1T26	39.18	51.70	9.12	100	-------	-----	100	-------	-----	Alpha	80
1T27	49.25	41.58	9.17	100	-------	-----	100	-------	-----	Epsilon	80
1T28	49.85	31.57	18.57	100	-------	-----	100	-------	-----	Alpha	80
1T33	59.42	31.36	9.22	100	-------	-----	100	-------	-----	Epsilon	80
1T34	69.70	21.02	9.28	100	-------	-----	100	-------	-----	Epsilon	80
1T36	80.10	10.57	9.33	100	-------	-----	100	-------	-----	Epsilon	80
[a]191	21.10	46.77	32.13	100	-------	-----	100	-------	Trace	Alpha	75
[a]192	50.10	26.51	23.38	100	-------	-----	100	Trace	-----	Alpha	75
[a]201	61.63	18.94	19.42	100	-------	-----	100	-------	-----	Alpha	75
[a]212	76.07	8.87	15.06	100	-------	-----	100	-------	-----	Alpha	75
213	91.5	-----	8.5	100	-------	-----	100	-------	-----	Epsilon	75
[a]225	89.06	-----	10.94	100	-------	-----	100	-------	-----	Epsilon	75
243	41	33	26	100	-------	-----	100	-------	-----	Alpha	75
262	23.5	44	32.5	100	-------	-----	100	-------	-----	Alpha	75
271	45.25	29.25	25.50	100	-------	-----	100	-------	-----	Alpha	75
300	82.5	5	12.5	100	-------	-----	100	Trace	-----	Epsilon	75
Alpha-plus-sigma alloys											
[a]104	-----	65.1	34.9	98	-------	2	99	-------	1	Alpha	75
172	16	37	47	18	-------	82	40	-------	60	Sigma	[b]95
[a]174	18.59	38.64	42.79	40	-------	60	50	-------	50	Alpha, sigma	[b]75
215	19.5	36	44.5	27	-------	73	25	-------	75	Alpha, sigma	200
[a]195	10.06	54.55	35.39	98	-------	2	100	-------	Trace	Alpha	75
216	10	41	49	15	-------	85	35	-------	65	Alpha, sigma	[b]200
217	17.5	45	37.5	78	-------	22	75	-------	25	Alpha, sigma	[b]75
218	22.98	43.16	33.86	95	-------	5	75	-------	25	Alpha, sigma	200
222	10	47	43	57	-------	43	50	-------	50	Alpha, sigma	[b]75
231	-----	46	54	7	-------	93	25	-------	75	Sigma	[b]200
241	15	37.5	47.5	16	-------	84	50	-------	50	Alpha, sigma	[b]200
[a]265	19.91	46.09	34.00	97	-------	3	100	-------	Trace	Alpha	75
[a]269	-----	44.75	55.25	3	-------	97	10	-------	90	Sigma	[b]240
[a]276	5.52	42.73	51.75	8	-------	92	5	-------	95	Sigma	[b]200
[a]278	9.88	54.8	35.32	98	-------	2	100	-------	Trace	Alpha	75
299	19.25	46.50	34.25	97	-------	3	99	-------	1	Alpha	88
318	22	44	34	94	-------	6	98	-------	2	Alpha	95
319	23.5	43.25	33.25	95	-------	5	100	-------	Trace	Alpha	95
Sigma alloys											
[a]101	10.86	35.54	53.60	-----	-------	100	-----	-------	100	Sigma	[b]75
[a]112	-----	43.3	56.7	-----	-------	100	-----	-------	100	Sigma	[b]200
221	5	38	57	-----	-------	100	-----	-------	100	Sigma	[b]200
226	10	38	52	-----	-------	100	(c)	(c)	(c)	----------	----
239	11	34	55	-----	-------	100	-----	-------	100	Sigma	[b]194
245	-----	41.5	58.5	-----	-------	100	-----	-------	100	Sigma	[b]200
279	10	34	56	-----	-------	100	-----	-------	100	Sigma	[b]164
281	4.44	38.3	57.2	-----	-------	100	-----	-------	100	Sigma	[b]200
286	16.5	33	50.5	-----	-------	100	(c)	(c)	(c)	----------	----
[a]287	15.70	34.02	50.28	-----	-------	100	-----	-------	100	Sigma	[b]164
[a]304	13.98	31.67	54.35	-----	-------	100	-----	-------	100	Sigma	[b]135
327	-----	40.5	59.5	-----	-------	100	-----	-------	100	Sigma	[b]115
[a]328	-----	44.06	55.94	-----	-------	100	-----	-------	100	Sigma	[b]95
[a]348	-----	40.44	59.56	-----	-------	100	-----	-------	100	Sigma	[b]95
357	17	33.5	49.5	-----	-------	100	(c)	(c)	(c)	----------	----
363	16	32.5	51.5	-----	-------	100	-----	?	98	Sigma	[b]95

[a]Chemical composition from analysis. Composition given for other alloys is as-weighed composition before melting.

[b]Not forged.

[c]Segregated.

TABLE III

DATA USED TO DETERMINE PHASE DIAGRAM FOR COBALT-CHROMIUM-IRON

SYSTEM AT 1200° C - Continued

Alloy	Weight percent			Phases from figure 1 (percent)			Phases found from - (percent)				Annealing time after forging (hr)
							Microstructure			X-ray	
	Fe	Co	Cr	Alpha	Epsilon	Sigma	Alpha	Epsilon	Sigma		
Epsilon-plus-sigma alloys											
[a]103	-----	27.9	72.1	-----	80	20	-----	95	5	Epsilon, sigma	[b]200
190	10	32	58	-----	65	35	(c)	(c)	(c)	----------	----
240	18	31.5	50.5	-----	50	50	(c)	(c)	(c)	----------	----
261	-----	31	69	-----	60	40	(c)	(c)	(c)	----------	----
277	5.16	36.72	58.12	-----	Trace	100	-----	5	95	Sigma	[b]194
[a]282	17.43	31.58	50.99	-----	10	90	-----	?	95	Sigma	[b]200
303	-----	26.5	73.5	-----	93	7	-----	5	95	----------	[b]135
[a]315	14.03	30.81	55.16	-----	90	10	-----	25	75	----------	[b]95
316	17.75	32.25	50	-----	Trace	100	(c)	(c)	(c)	----------	----
345	19	31.5	49.5	-----	100	Trace	(c)	(c)	(c)	----------	----
346	17	32	51	-----	Trace	100	-----	Trace ?	99	Sigma	[b]95
347	15.5	30.5	54	-----	25	75	(c)	(c)	(c)	----------	----
349	5	32	63	-----	70	30	-----	60	40	Alpha, epsilon, sigma	[b]95
[a]356	5.39	30.53	64.08	-----	92	8	-----	95	5	Epsilon, sigma	[b]95
[a]359	-----	39.45	60.55	-----	5	95	-----	5	95	Sigma	[b]95
365	10	31	59	-----	95	5	-----	-------	-----	----------	----
Epsilon alloys											
1T11	24.22	25.88	49.40	-----	100	-----	-----	100	-----	Sigma	[b]200
1T23	43.03	21.11	35.84	-----	100	-----	-----	100	-----	Alpha, epsilon	111
[a]110	40.5	22.04	37.46	-----	100	-----	-----	100	-----	Alpha, epsilon	111
[a]142	16.17	27.27	56.56	-----	100	-----	-----	100	-----	Epsilon	[b]194
[a]154	30.63	39.14	30.22	-----	100	-----	-----	100	-----	Epsilon	111
180	10	26	64	-----	100	-----	-----	100	-----	Epsilon	[b]150
181	24	24	52	-----	100	-----	-----	100	-----	Epsilon	[b]150
185	27.5	24.5	48	-----	100	-----	-----	100	-----	Epsilon	[b]75
187	27.5	27	45.5	-----	100	-----	-----	100	-----	Alpha, epsilon	[b]200
219	5	23.5	66.5	-----	100	-----	-----	100	-----	----------	[b]115
220	15	29	56	-----	100	-----	-----	100	-----	Epsilon, sigma	[b]194
242	22.5	30.5	47	-----	100	-----	-----	100	-----	Epsilon, sigma	[b]200
244	37	-----	13	-----	100	-----	-----	100	-----	Epsilon	75
[a]267	49.47	20.03	30.13	-----	100	-----	-----	100	-----	Alpha, epsilon	75
268	86.27	-----	13.73	-----	100	-----	-----	100	-----	Epsilon	75
274	17	29	54	-----	100	-----	-----	100	-----	Epsilon, sigma	[b]200
283	19	28.75	52.25	-----	100	-----	(c)	(c)	(c)	----------	----
284	26.5	28	45.5	-----	100	-----	(c)	(c)	(c)	----------	----
285	19	30	51	-----	100	-----	-----	100	-----	Epsilon, sigma	[b]164
290	75	7.5	17.5	-----	100	-----	10	90	-----	----------	95
291	61	14.5	24.5	-----	100	-----	-----	100	-----	----------	75
293	35	24.75	40.25	-----	100	-----	(c)	(c)	(c)	----------	----
[a]294	17.49	28.34	54.16	-----	100	-----	-----	100	-----	Epsilon, sigma	[b]240
[a]295	9.94	28.99	61.07	-----	100	-----	-----	100	-----	Epsilon, sigma	[b]240
301	32.5	24.5	43	-----	100	-----	(c)	(c)	(c)	----------	----
[a]302	77.60	6.25	16.15	-----	100	-----	-----	100	-----	Epsilon	88
305	25	27.5	47.5	-----	100	-----	-----	100	-----	Epsilon	[b]135
309	31	26.75	42.25	-----	100	-----	Trace	100	-----	----------	----
310	20	31	49	-----	100	-----	(c)	(c)	(c)	----------	----
[a]325	88.10	-----	11.82	-----	100	-----	-----	100	-----	----------	115
326	10	30.25	59.75	-----	100	-----	-----	100	-----	----------	115
317	18.5	31	50.5	-----	100	-----	(c)	(c)	(c)	----------	----
353	46	21.25	32.75	-----	100	-----	-----	100	-----	Alpha, epsilon	95

[a]Chemical composition from analysis. Composition given for other alloys is as-weighed composition before melting.

[b]Not forged.

[c]Segregated.

TABLE III

DATA USED TO DETERMINE PHASE DIAGRAM FOR COBALT-CHROMIUM-IRON

SYSTEM AT 1200° C - Concluded

Alloy	Weight percent			Phases from figure 1 (percent)			Phases found from - (percent)				Annealing time after forging (hr)
							Microstructure			X-ray	
	Fe	Co	Cr	Alpha	Epsilon	Sigma	Alpha	Epsilon	Sigma		
Alpha-plus-epsilon alloys											
1T24	40.81	30.97	28.22	80	20	-----	80	20	-----	Alpha, epsilon	75
[a]1T29	51.18	23.42	25.40	70	30	-----	50	50	-----	Alpha, epsilon	75
[a]107	47.08	32	20.9	5	95	-----	5	95	-----	Alpha, epsilon	[b]95
[a]108	29.44	27.66	42.9	2	98	-----	-----	100	-----	Alpha, epsilon	[b]200
[a]109	35.07	27.82	37.11	25	95	-----	20	80	-----	Alpha, epsilon	[b]150
[a]151	30.67	38.85	30.49	95	5	-----	98	2	-----	Alpha	75
[a]157	28.70	30.44	40.85	20	80	-----	(c)	(c)	(c)	----------	----
[a]158	31.12	29.42	39.46	22	78	-----	20	80	-----	Alpha, epsilon	[b]95
[a]165	26.46	34.10	39.43	45	55	-----	50	50	-----	Alpha, epsilon, sigma	[b]150
166	36	30	34	40	60	-----	5	95	-----	Alpha, epsilon, sigma	200
[a]167	33.98	35.04	30.98	78	22	-----	70	30	-----	Alpha, epsilon	[b]75
[a]173	22.45	34.41	43.14	29	71	-----	35	65	-----	Alpha	[b]157
[a]175	26.25	36.36	37.39	55	45	-----	40	60	-----	Alpha	[b]200
176	30	36	34	60	40	-----	60	40	-----	Alpha, epsilon	75
177	27	39	34	80	20	-----	65	35	-----	Alpha, epsilon	[b]200
186	26	30	44	16	84	-----	(c)	(c)	(c)	----------	194
196	50	24.5	25.5	80	20	-----	70	30	-----	Alpha	75
[a]204	24.45	31.00	44.54	10	90	-----	(c)	(c)	(c)	----------	----
[a]224	76.24	8.28	15.48	80	20	-----	50	50	-----	----------	75
228	35	26	39	7	93	-----	5	95	-----	Alpha, epsilon	[b]200
[a]229	43.35	22.58	34.06	5	95	-----	10	90	-----	Alpha, epsilon	200
230	61	17.5	21.5	70	30	-----	65	35	-----	Alpha, epsilon	75
244	87	13	-----	-----	100	-----	-----	100	-----	Epsilon	75
263	61	16	23	33	67	-----	20	80	-----	Alpha, epsilon	75
264	32.5	29.25	38.25	25	75	-----	(c)	(c)	(c)	----------	----
266	31.75	28.6	39.65	16	84	-----	30	70	-----	Alpha, epsilon	87
267	50	20	30	-----	100	-----	-----	100	-----	Alpha, epsilon	75
270	56	21.25	22.75	95	5	-----	-----	Trace	-----	Alpha	75
275	36	35.5	28.5	98	2	-----	100	Trace	-----	Alpha	75
292	50	19	31	-----	100	-----	70	30	-----	----------	75
306	26.75	29.5	43.75	2	98	-----	(c)	(c)	(c)	----------	----
307	27.5	30	42.5	10	90	-----	5	95	-----	Alpha, epsilon	[b]95
319	23.5	43.25	33.25	98	2	-----	100	Trace	-----	Alpha	----
324	81	4.75	14.75	10	90	-----	10	90	-----	----------	115
329	50	21.25	28.75	33	67	-----	35	65	-----	Alpha, epsilon	----
342	25.5	32.75	41.75	25	75	-----	5	95	-----	Alpha, epsilon	[b]95
343	25	31.75	43.25	12	88	-----	40	60	-----	Alpha, epsilon	[b]95
344	24	33	43	25	75	-----	10	90	-----	Alpha, epsilon	[b]95
350	76	7.5	16.5	16	84	-----	40	60	-----	Epsilon	95
351	68.5	11.75	19.75	33	67	-----	40	60	-----	Epsilon	95
352	68.5	13.25	18.25	90	10	-----	100	Trace	-----	Alpha, epsilon	95
355	26.5	32	41.5	25	75	-----	10	90	-----	Alpha, epsilon	[b]95
369	23.25	32.5	44.25	17	83	-----	15	85	-----	Alpha	[b]95
374	24	35.5	40.5	45	55	-----	(c)	(c)	(c)	----------	----
Alpha-plus-epsilon-plus-sigma alloys											
358	19	32.5	48.5	5	15	80	(c)	(c)	(c)	----------	----
367	20.25	33.75	46	10	45	45	10	?	Matrix	Alpha, epsilon	[b]95
368	21	35	44	15	42	43	10	?	Matrix	Alpha, epsilon	[b]95
373	22	37.5	40.5	35	33	33	40	-------	60	Alpha, sigma	[b]95

[a]Chemical composition from analysis. Composition given for other alloys is as-weighed composition before melting.

[b]Not forged.

[c]Segregated.

TABLE IV

RESULTS OF CARBON ANALYSES

Alloy	Weight percent				
	Fe	Co	Cr	Ni	C
3-top	-----	44.98	42.80	11.45	0.03
3-bottom	-----	45.65	42.19	11.85	.05
4-top	-----	36.76	47.49	14.66	.03
4-bottom	-----	37.30	47.66	14.92	.03
5	-----	25.43	52.55	13.83	.02
7-bottom	-----	17.01	66.21	13.17	.03
19	-----	8.53	74.50	15.06	.04
23	-----	40.65	51.08	7.98	.03
24	-----	33.48	57.28	8.35	.12
25	-----	18.66	69.29	11.10	.02
212-bottom	76.00	8.86	15.04	-----	.05
224-bottom	76.20	8.28	15.47	-----	.05

NACA

TABLE V

θ VALUES OF X-RAY DIFFRACTION LINES OTHER THAN ALPHA LINES APPEARING IN X-RAY DIFFRACTION PATTERNS OF ALLOYS QUENCHED TO ROOM TEMPERATURE FROM ALPHA PHASE REGION AT 1200° C

[Each line measured once; unfiltered chromium radiation]

Alloy	θ values (deg)							
IT1	-----	30.71	-----	31.77	-----	33.76	-----	-----
IT2	-----	-----	30.81	31.70	-----	-----	34.27	36.57
IT3	-----	-----	30.78	31.67	32.78	-----	34.27	36.51
IT13	-----	30.52	-----	31.49	-----	-----	34.01	36.42
IT15	-----	-----	-----	31.67	32.89	-----	-----	36.56
IT17	-----	-----	30.83	31.67	32.78	-----	34.25	36.54
IT25	-----	-----	-----	-----	32.75	33.07	34.28	36.56
IT26	-----	-----	-----	31.18	-----	-----	34.68	-----
IT28	-----	-----	-----	31.38	-----	34.02	34.28	36.30
104	-----	-----	-----	31.53	-----	-----	-----	36.44
151	-----	-----	-----	31.26	32.46	33.79	-----	36.10
191	-----	-----	-----	31.04	-----	-----	34.47	-----
192	-----	30.40	-----	31.30	-----	-----	-----	36.16
201	-----	-----	-----	-----	-----	-----	34.44	-----
212	27.53	-----	-----	31.38	-----	-----	34.06	38.66
243	-----	-----	-----	31.33	-----	-----	34.41	36.33
262	-----	30.60	-----	31.54	-----	-----	34.05	36.37
265	-----	-----	-----	31.60	32.80	-----	-----	36.43
270	-----	-----	-----	31.54	-----	34.12	34.56	36.41
271	28.37	30.60	-----	31.52	-----	-----	34.05	36.34
275	-----	30.60	30.86	31.47	-----	34.42	34.01	37.14
278	-----	-----	30.78	-----	32.04	-----	34.21	-----
318	-----	-----	30.92	31.49	32.03	32.64	34.29	36.45
319	-----	-----	-----	31.49	32.64	-----	34.05	36.30

NACA

TABLE VI

COMPOSITIONS OF ALLOYS USED IN PLOTTING BOUNDARIES OF SIGMA PHASE

IN COBALT-CHROMIUM-IRON SYSTEM AT 800° C

[Data for fig. 16]

Alloy	Weight percent			Annealing time at 800° C (hr)	Second phase present in sigma matrix
	Fe	Co	Cr		
[a]1T7	11.39	45.69	42.91	Approx. 48	Yes[b]
1T11	20.36	32.23	47.41	Approx. 48	No
1T20	30.71	21.61	47.68	Approx. 48	No
1T22	41.18	10.87	47.95	Approx. 48	No
1T30	51.12	10.79	38.09	85	Yes[c]
[a]101	10.86	35.54	53.60	Approx. 48	No
[a]107	20.9	32.00	47.08	Approx. 48	No
[a]108	29.44	27.66	42.9	60	No
[a]110	40.5	22.04	37.46	60	Yes[c]
[a]111	34.49	24.11	41.40	60	No
140	30	16	54	60	Yes[c]
141	40	6	54	Approx. 48	Yes[c]
[a]142	16.17	27.27	56.56	65	No
215	19.5	36	44.5	88	Yes
216	10	41	49	88	Yes
[a]269	-----	44.75	55.25	90	Yes[b]
[a]277	5.16	36.72	58.12	65	No
279	10	34	56	85	No
[a]294	17.49	28.34	54.16	85	No
326	10	30.25	59.75	65	Yes[c]
[a]328	-----	44.06	55.94	90	No
344	24	33	43	65	Yes
[a]348	-----	40.44	59.56	90	Yes
[a]359	-----	39.45	60.55	90	Yes[c]
364	44.25	16	39.75	150	No

[a]Chemical composition from chemical analysis. Composition given for other alloys is weighed composition before melting.

[b]Probably beta.

[c]Probably epsilon.

TABLE VII

COMPOSITIONS AND PHASES OF ALLOYS USED IN PLOTTING ALPHA AND BETA PHASE BOUNDARIES IN COBALT-CHROMIUM-NICKEL SYSTEM AT 900° C

Alloy	Composition by weight percent			Microscopic results		Annealing schedule after double-forging	
	Co	Cr	Ni	Matrix	Second phase (percent)	Time (hr)	Temperature (°C)
123	60	34	6	Alpha	[a]1	48	900
124	46	34	20	Alpha	--------	48	880
130	28	38	34	Alpha	[b]2	48	950
162	54	36	10	Alpha	[a]Trace	48	885
[c]168	17.49	40.29	42.21	Alpha	[b]3	48	940
208	-----	38.5	61.5	Alpha	--------	48	875
209	65.5	32.5	2	Beta	--------	72	900
210	42	34	24	Alpha	--------	48	875
211	22	38	40	Alpha	[b]3	48	902
[c]232	60.99	32.64	6.37	Alpha	--------	86	900
233	10	40	50	Alpha	[b]1	86	900
234	13	37	50	Alpha	--------	86	900
235	25	35	40	Alpha	--------	86	900
236	31.5	34.5	34	Alpha	--------	86	900
[c]237	39.31	36.16	24.53	Alpha	--------	86	900
[c]238	74.77	25.23	-----	Alpha	20 beta	86	905
254	70	30	-----	Beta	--------	180	900
[c]255	73.32	24.89	1.79	Alpha	--------	86	905
[c]256	68.02	29.59	2.39	Beta	--------	86	896
257	66	30	4	Alpha	--------	86	900
[c]258	63.95	30.98	5.07	Alpha	--------	180	900
[c]259	66.71	26.78	6.51	Alpha	--------	86	896
333	55	35	10	Alpha	[a]3	72	900
334	50	34.5	15.5	Alpha	[b]1	72	900
335	63	33	4	Alpha	[a]1, [d]1	72	900
336	60	35.5	4.5	Alpha	[a]5	72	900
337	56	33	11	Alpha	--------	72	900
338	59	32	9	Alpha	[a]Trace	84	900
339	50	33	17	Alpha	--------	84	900
340	70	28	2	Alpha	--------	84	900
[c]341	66.49	33.51	-----	Alpha	[a]5 to 10	84	900

[a]Probably sigma.
[b]Probably epsilon.
[c]Chemical composition from analysis. Composition of other alloys from as-weighed composition.
[d]Probably beta.

TABLE VIII

DATA FOR PRELIMINARY SURVEY OF ALPHA AND BETA PHASE BOUNDARIES

IN COBALT-CHROMIUM-NICKEL ALLOYS AT 900° C

Annealing temperature (°C)	Annealing time (hr) after double-forging for alloys[1] - (2)				
	123	124	130	162	168
770	--------	24 - Yes	12 - Yes	--------	--------
780	12 - Yes	12 - No	--------	--------	--------
830	--------	24 - No	--------	48 - Yes	--------
885	--------	--------	--------	48 - Yes	--------
900	48 - No	12 - No	--------	--------	--------
930	48 - No	--------	--------	--------	48 - Yes
950	48 - No	48 - No	48 - Yes	48 - No	--------
990	12 - No	48 - No	48 - No	48 - No	48 - Yes
1015	--------	--------	--------	--------	48 - Yes
1040	--------	--------	--------	--------	48 - No

[1]Composition of alloys given in table VII.

[2]"Yes" or "No" indicates presence of second phase in microstructure.

TABLE IX

COMPOSITIONS AND PHASES FOR ALLOYS USED IN PLOTTING ALPHA PHASE BOUNDARIES

IN COBALT-CHROMIUM-IRON-NICKEL SYSTEM

Alloy	Composition by weight percent				Phases found from - (percent)				Annealing time at 1200° C after forging (hr)
	Fe	Co	Cr	Ni	Microstructure			X-ray	
					Alpha	Epsilon	Sigma		
10 percent iron									
[a]125	9.53	14.94	40.32	35.21	100	Trace	-----	----------	13
[a]126	9.31	16.68	37.66	36.35	100	-----	-----	----------	13
[a]131	11.06	34.26	36.66	18.02	100	-----	-----	----------	13
133	10	46.8	41.4	1.8	100	-----	-----	Alpha, sigma	13
[a]135	10.69	1.87	41.48	45.94	99	1	-----	----------	13
[a]136	10.28	9.73	39.72	40.27	100	-----	-----	----------	13
[a]137	10.55	23.87	28.30	27.28	100	-----	-----	----------	13
[a]138	10.20	24.25	37.02	28.53	100	-----	-----	----------	13
145	10	50.57	36.67	2.25	97	-----	3	----------	75
[a]146	10.37	40.01	36.50	13.12	100	-----	-----	----------	13
[a]147	10.62	54.99	34.01	.37	100	-----	-----	----------	13
[a]150	10.70	46.18	35.17	7.61	100	-----	-----	----------	13
169	10	16.2	43.2	30.6	85	15	-----	Alpha, epsilon	13
170	10	13.5	43.2	33.3	80	20	-----	Alpha, epsilon	75
193	10	23.4	42.75	23.85	75	25	-----	Alpha, epsilon	75
194	10	29.7	42.3	18	75	25	-----	Alpha, epsilon	75
200	10	38.7	41.4	9.9	80	-----	20	Alpha, sigma	75
[a]205	10.39	47.61	36.16	5.84	98	-----	2	Alpha	13
[a]206	10.49	31.10	38.96	19.45	95	5	-----	Alpha	13
[a]207	10.47	22.74	38.49	28.30	99	1	-----	Alpha	13
214	10	34.2	40.5	15.3	85	-----	15	Alpha, epsilon, sigma	75
[a]249	10	-----	48.6	41.4	40	60	-----	Alpha, epsilon	75
278	9.88	54.80	35.32	-----	100	-----	Trace	Alpha	75
20 percent iron									
149	20	41.6	36.8	1.6	80	-----	20	Alpha, epsilon, sigma	75
[a]152	20.58	46.06	33.03	.32	100	-----	-----	----------	85
[a]153	21.15	33.41	32.25	13.09	100	-----	-----	----------	13
[a]155	19.47	25.13	35.35	20.05	98	2	-----	----------	13
156	20	33.6	34.8	11.6	95	5	-----	----------	13
[a]159	20.70	15.98	35.42	27.89	100	Trace	-----	----------	13
[a]160	21.13	9.47	38.03	31.37	100	Trace	-----	----------	75
[a]161	20.63	2.00	35.50	41.86	100	-----	-----	----------	13
[a]164	21.20	45.37	32.39	1.03	100	-----	Trace	----------	75
246	20	15.2	40.8	24	60	40	-----	----------	[b]86
247	20	24.8	39.2	16	65	35	-----	Alpha, epsilon	[b]86
251	20	2.4	45.6	32	50	50	-----	Alpha, epsilon	[b]86
260	20	33.6	38.4	8	70	30	-----	Alpha, epsilon	[b]86
[a]265	19.91	46.09	34.00	-----	100	-----	Trace	Alpha	75
30 percent iron									
[a]151	30.67	38.85	30.49	-----	98	2	-----	----------	75
[a]179	30.78	24.58	30.96	13.67	100	Trace	-----	----------	13
[a]183	30.14	30.68	30.20	8.98	100	Trace	-----	----------	13
[a]184	30.78	18.05	31.04	20.43	100	Trace	-----	----------	13
[a]188	30.69	9.69	33.72	25.98	100	Trace	-----	----------	75
[a]189	29.92	-----	36.41	33.67	92	8	-----	----------	75
[a]197	30.58	1.47	33.07	34.89	100	-----	-----	----------	75
[a]198	30.52	36.78	29.97	2.72	100	Trace	-----	----------	75
199	30	31.5	35.7	.8	60	40	-----	Alpha, epsilon	75
248	30	17.5	38.5	14	50	50	-----	Alpha, epsilon	[b]86
252	30	-----	39.9	30.1	70	30	-----	Alpha, epsilon	[b]86

[a]Chemical composition from analysis. Composition of other alloys from as-weighed composition before melting.

[b]Not forged.

TABLE X

DATA USED IN PLOTTING MAXIMUM SOLUBILITY AT 1200° C OF CHROMIUM IN ALPHA PHASE OF COBALT-CHROMIUM-IRON-NICKEL ALLOYS

[See fig. 26]

Weight percent		Maximum chromium in alpha solid solution; weight percent
Fe	Co	
0	0	42.2
0	10	44.3
0	20	43.4
0	30	40.8
0	40	38.6
0	50	37
0	60	35
0	66	34
10	0	42.3
10	9	40
10	18	38.7
10	27	38.25
10	36	37.3
10	45	36
10	54.9	35.1
20	0	40
20	8	38
20	16	36
20	24	34.8
20	32	34
20	40	33.2
20	46.4	33.6
30	0	35.7
30	7	34.3
30	14	32.9
30	21	31.9
30	28	30.6
30	35	30.3
30	39.9	30.1

NACA

TABLE XI

DETERMINATION BY X-RAY DIFFRACTION OF ALPHA CORNER OF THREE-PHASE FIELD IN COBALT-CHROMIUM-IRON-NICKEL ALLOYS CONTAINING 10 PERCENT IRON

[Data for fig. 27]

Alloy	Weight percent Co ± 0.9	Extrapolated value of a_o (A)
169	18	3.5784
193	26	3.5776
194	33	3.5773
200	47	3.5698
205	53	3.5666
206	36	3.5743
207	24.5	3.5740
214	40	3.5712
249	0	3.5803

NACA

TABLE XII

θ VALUES OF X-RAY DIFFRACTION LINES ASSOCIATED WITH

Z PHASE FROM DIFFRACTION PATTERN OF ALLOY 194

[X-ray powder filed, annealed 10 min at 1200° C, and then quenched in cold tap water; unfiltered chromium radiation]

Alloy	θ
194	25.42
	27.45
	28.72
	30.57
	31.78
	34.01
	37.37

TABLE XIII

1200° C DATA FROM COBALT-CHROMIUM-IRON TERNARY SYSTEM

BY KOSTER (REFERENCE 12)

[Data for fig. 30]

Weight percent Fe	Limit of alpha phase; weight percent Cr	Limit of epsilon phase; weight percent Cr
30	27.8	38.2
40	25.8	34
45	23.32	31.3
50	25	29.5
60	21.4	23.2
70	18.9	20.5
80	14.4	15.64
85	12.06	13.13
90	8.2	9.1

NACA

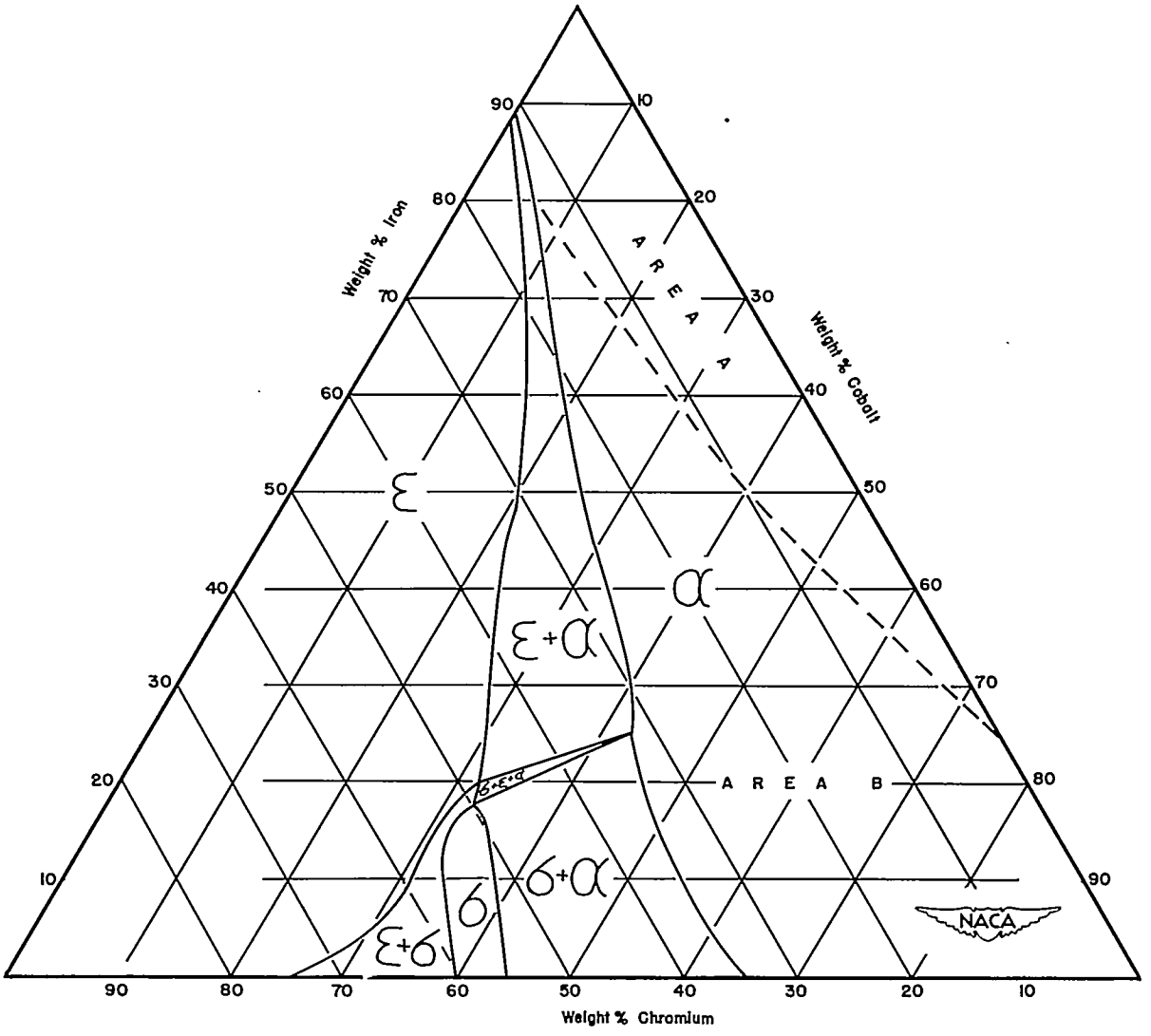

Figure 1.- 1200° C isothermal section of cobalt-chromium-iron ternary system.

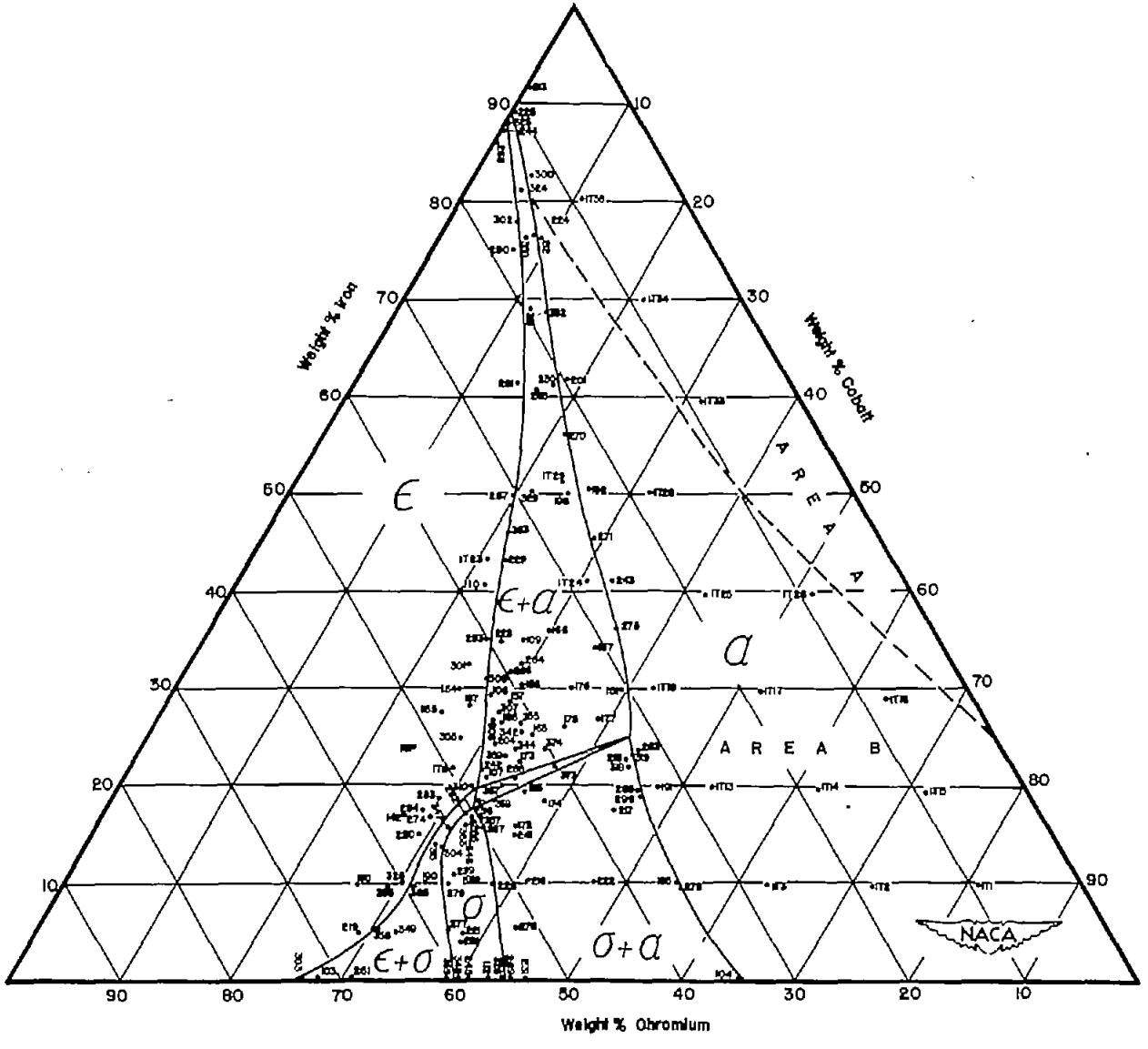

Figure 2.- 1200° C isothermal section of cobalt-chromium-iron system with chemical composition of alloys (see table III).

Figure 3.- Alloy 212 containing 76.07 percent iron, 8.87 percent cobalt, and 15.06 percent chromium. Electrolytically polished and etched with reagent 1; microstructure is typical of area A, figure 1; X200.

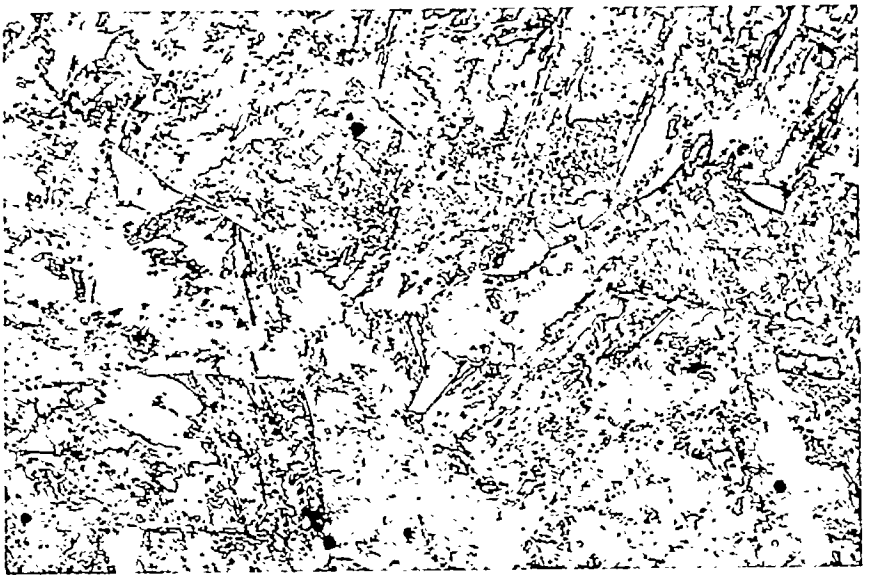

Figure 4.- Alloy 300 containing 82.5 percent iron, 5 percent cobalt, and 12.5 percent chromium. Electrolytically polished and etched with reagent 1; particles of epsilon phase in a transformed alpha matrix; X200.

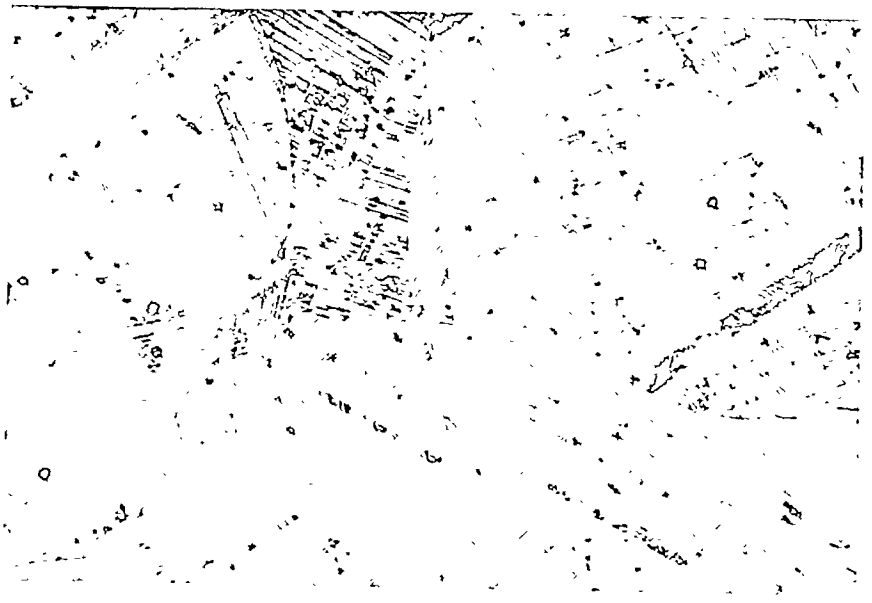

Figure 5.- Alloy 1T15 containing 19.38 percent iron, 71.59 percent cobalt, and 9.03 percent chromium. Electrolytically polished and etched with reagent 1; typical structure of alloy in area B, figure 1; X200.

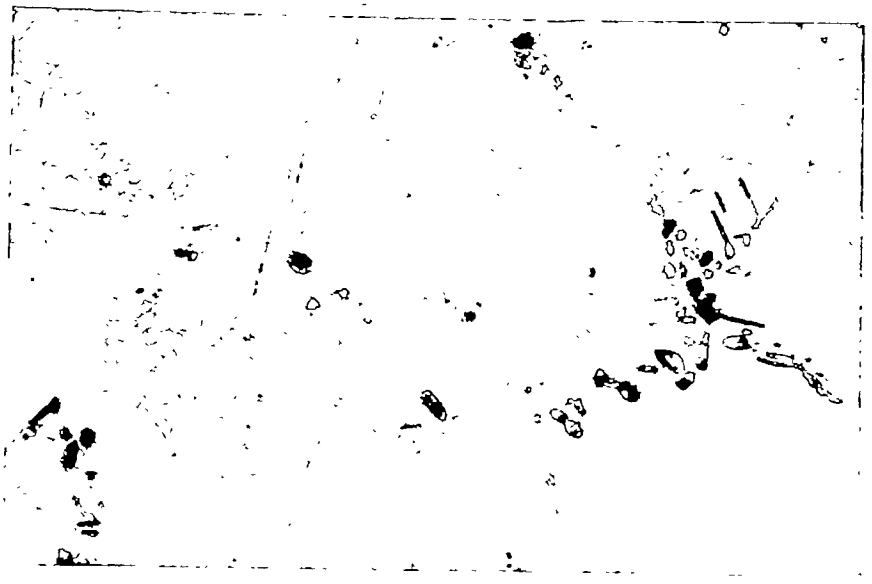

Figure 6.- Alloy 104 containing 65.1 percent cobalt and 34.9 percent chromium. Electrolytically polished and etched with reagent 1; typical structure of alloy in area B, figure 1; X400.

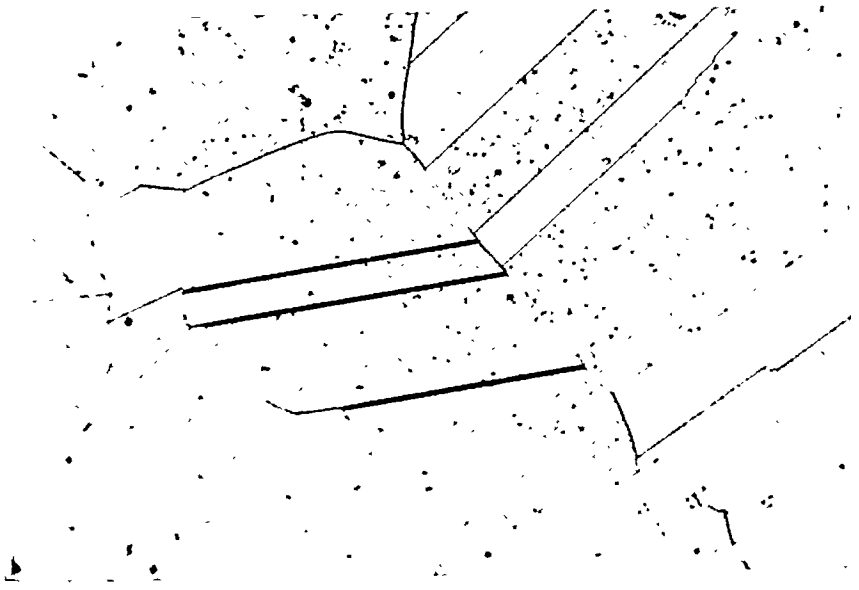

Figure 7.- Alloy 1T16 containing 29 percent iron, 63.5 percent cobalt, and 7.5 percent chromium. Electrolytically polished and etched with reagent 1; structure of an alloy located in area B, figure 1, which did not transform when quenched from 1200° C to room temperature; X200.

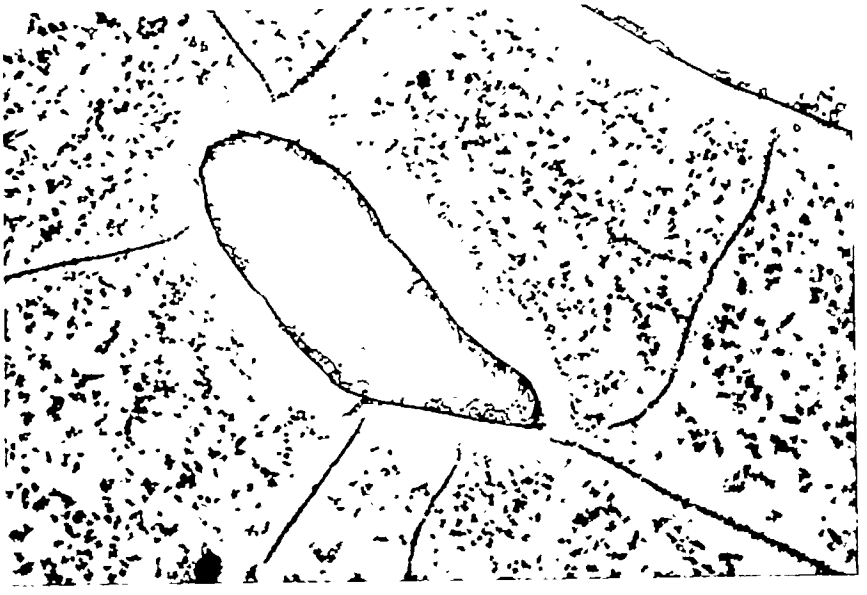

Figure 8.- Alloy 173 containing 22.45 percent iron, 34.41 percent cobalt, and 43.14 percent chromium. Electrolytically polished and etched with reagent 2; alpha-phase particles in matrix of epsilon phase with sigma precipitate; precipitate is not revealed near boundary of alpha-phase particle; X750.

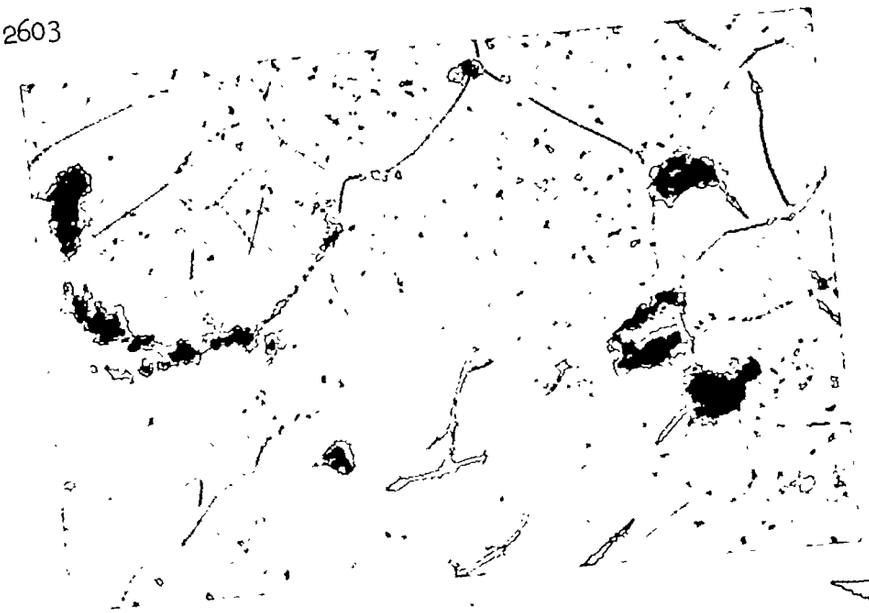

Figure 9.- Alloy 356 containing 5.39 percent iron, 30.53 percent cobalt, and 64.08 percent chromium. Electrolytically polished and etched with reagent 2; cracked particles of sigma phase in epsilon-phase matrix with a sigma-phase precipitate, which is not revealed near boundaries of primary particles of sigma phase; X500.

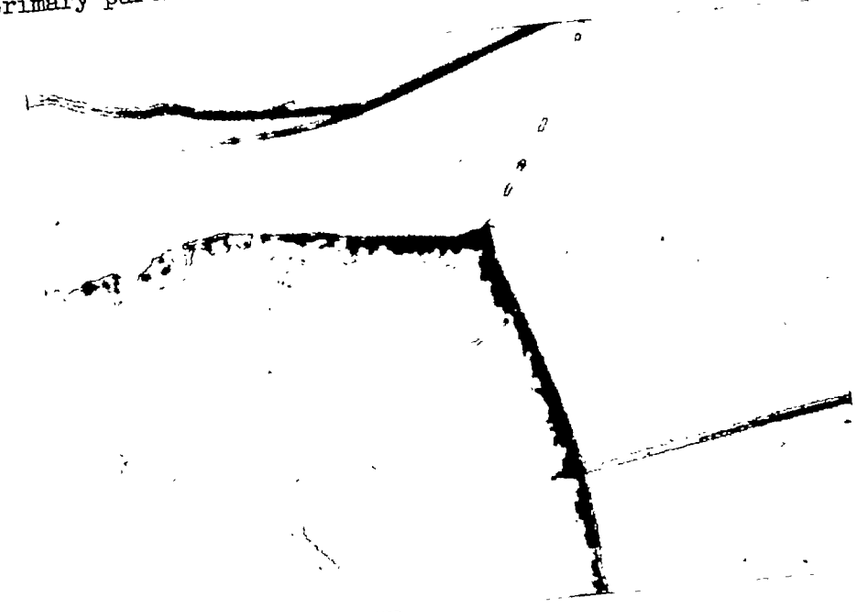

Figure 10.- Alloy 277 containing 5.16 percent iron, 36.72 percent cobalt, and 58.12 percent chromium. Electrolytically polished and etched with reagent 2; structure of intermediate layer existing between cracked sigma-phase matrix and a particle of epsilon phase with sigma-phase precipitate; X4000.

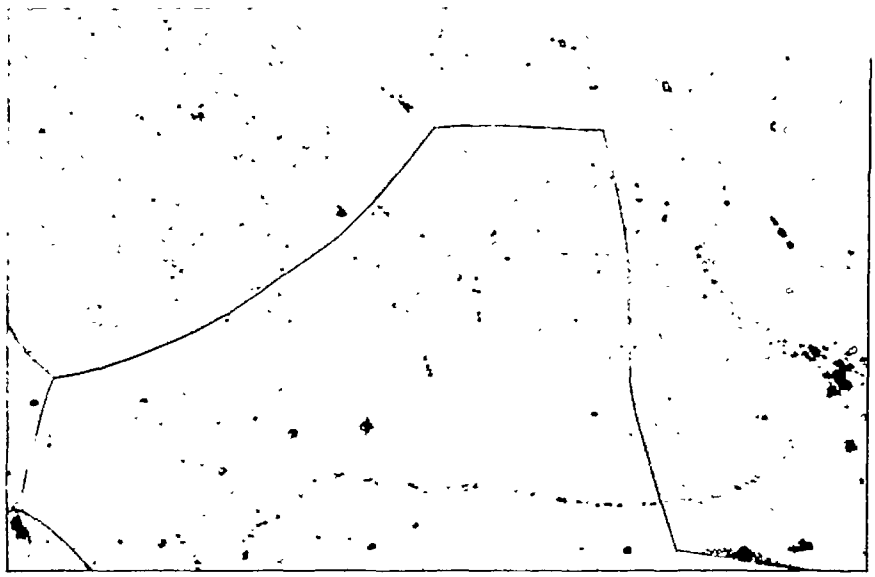

Figure 11.- Alloy 325 containing 88.18 percent iron and 11.82 percent chromium. Electrolytically polished and etched with reagent 1; typical structure of epsilon phase alloys with high iron contents quenched from 1200° C to room temperature; X400.

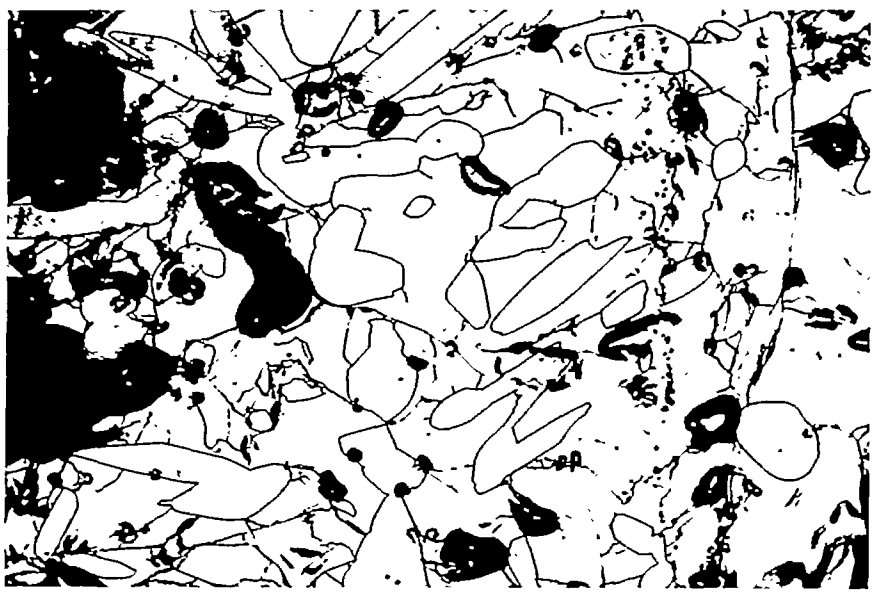

Figure 12.- Alloy 373 containing 22 percent iron, 37.5 percent cobalt, and 40.5 percent chromium. Electrolytically polished and etched with reagent 1; cracked sigma-phase matrix containing alpha-phase particles; striations in alpha phase are revealed; X200.

Figure 13.- Alloy 359 containing 39.45 percent cobalt and 60.55 percent chromium. Electrolytically polished and etched with reagent 2; small particles of epsilon phase in a cracked sigma-phase matrix; X750.

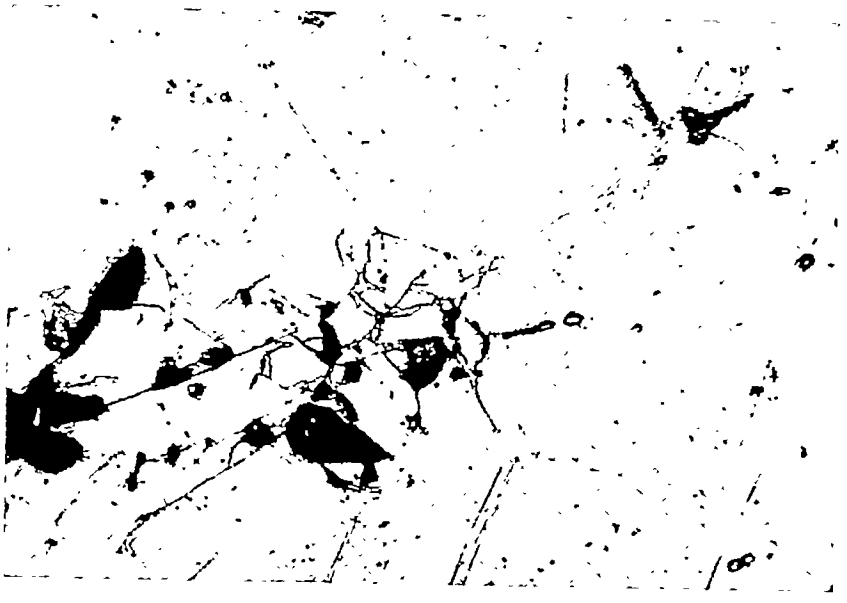

Figure 14.- Alloy 294 containing 17.49 percent iron, 28.34 percent cobalt, and 54.16 percent chromium. Electrolytically polished and etched with reagent 2; "clotlike" particle of segregated second phase, probably sigma phase, in an epsilon-phase matrix with sigma-phase precipitate; X200.

Figure 15.- Alloy 368 containing 21 percent iron, 35 percent cobalt, and 44 percent chromium. Electrolytically polished and etched with reagent 2; an alpha-phase particle in a cracked sigma-phase matrix containing a fine dispersion of another phase, probably epsilon phase; X750.

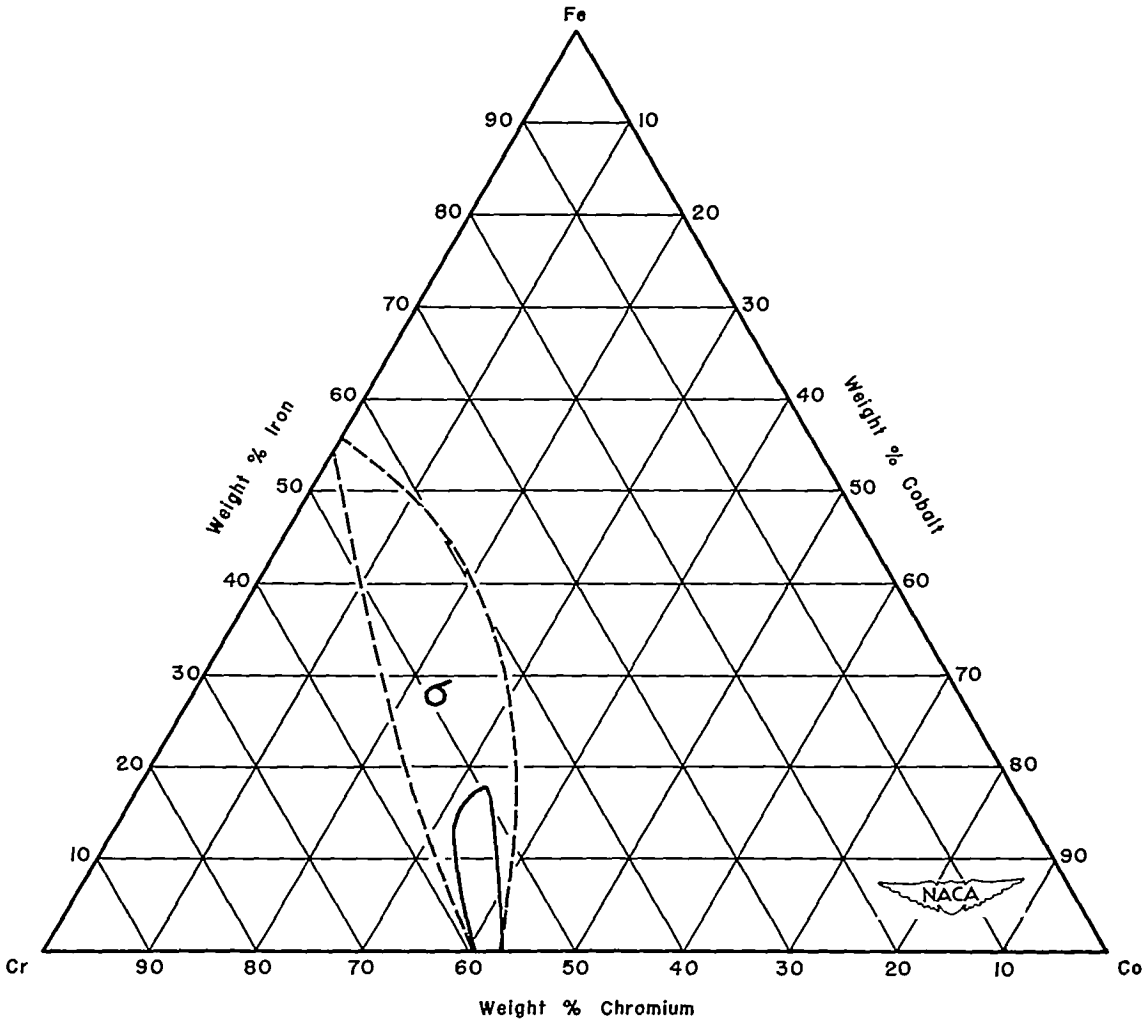

Figure 16.- Boundaries of sigma phase in cobalt-chromium-iron system at 800° C (dashed lines). Solid line indicates boundaries of sigma phase at 1200° C.

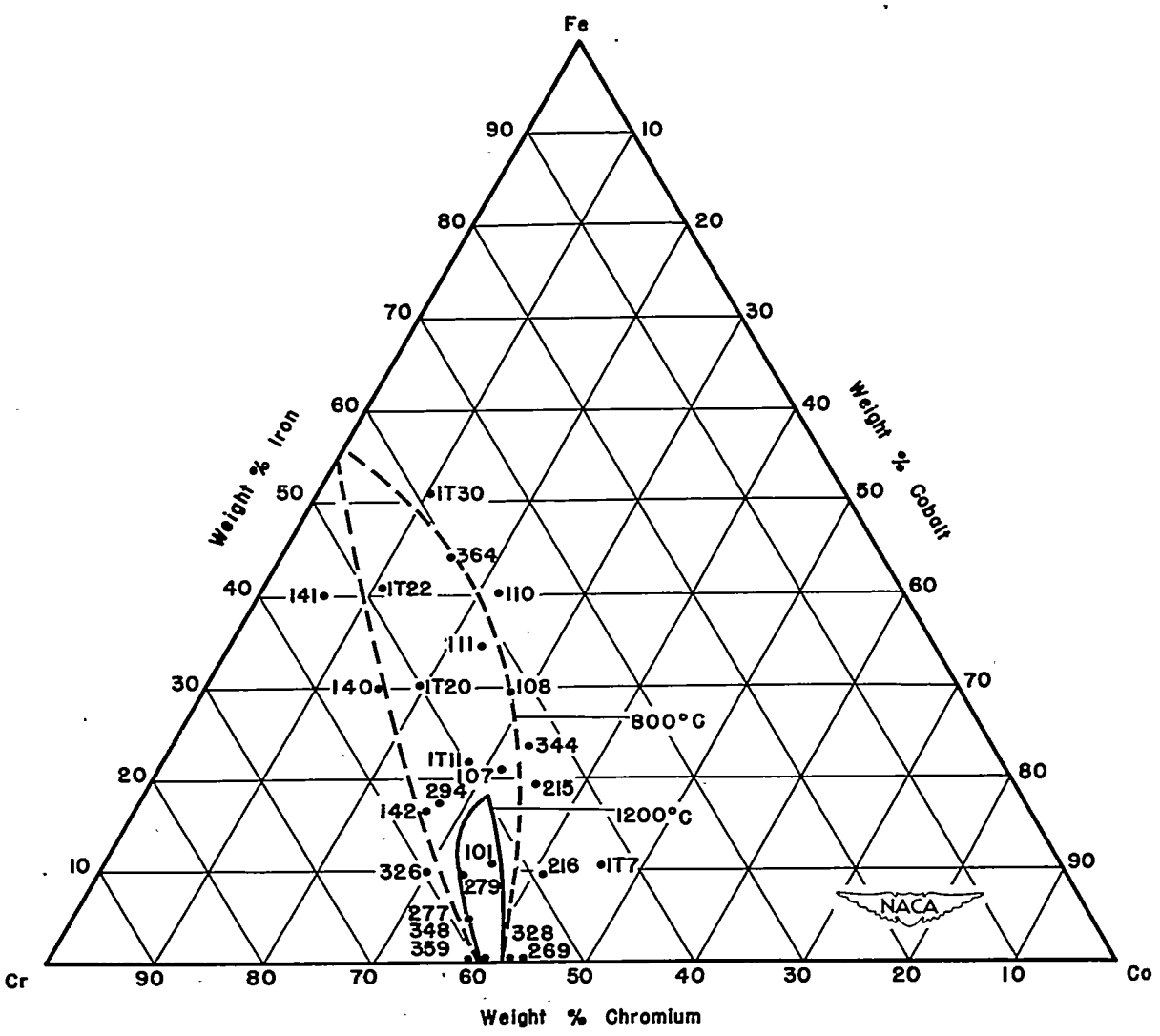

Figure 17.- Boundaries of sigma phase at 800° C and 1200° C with composition of alloys (see table VI).

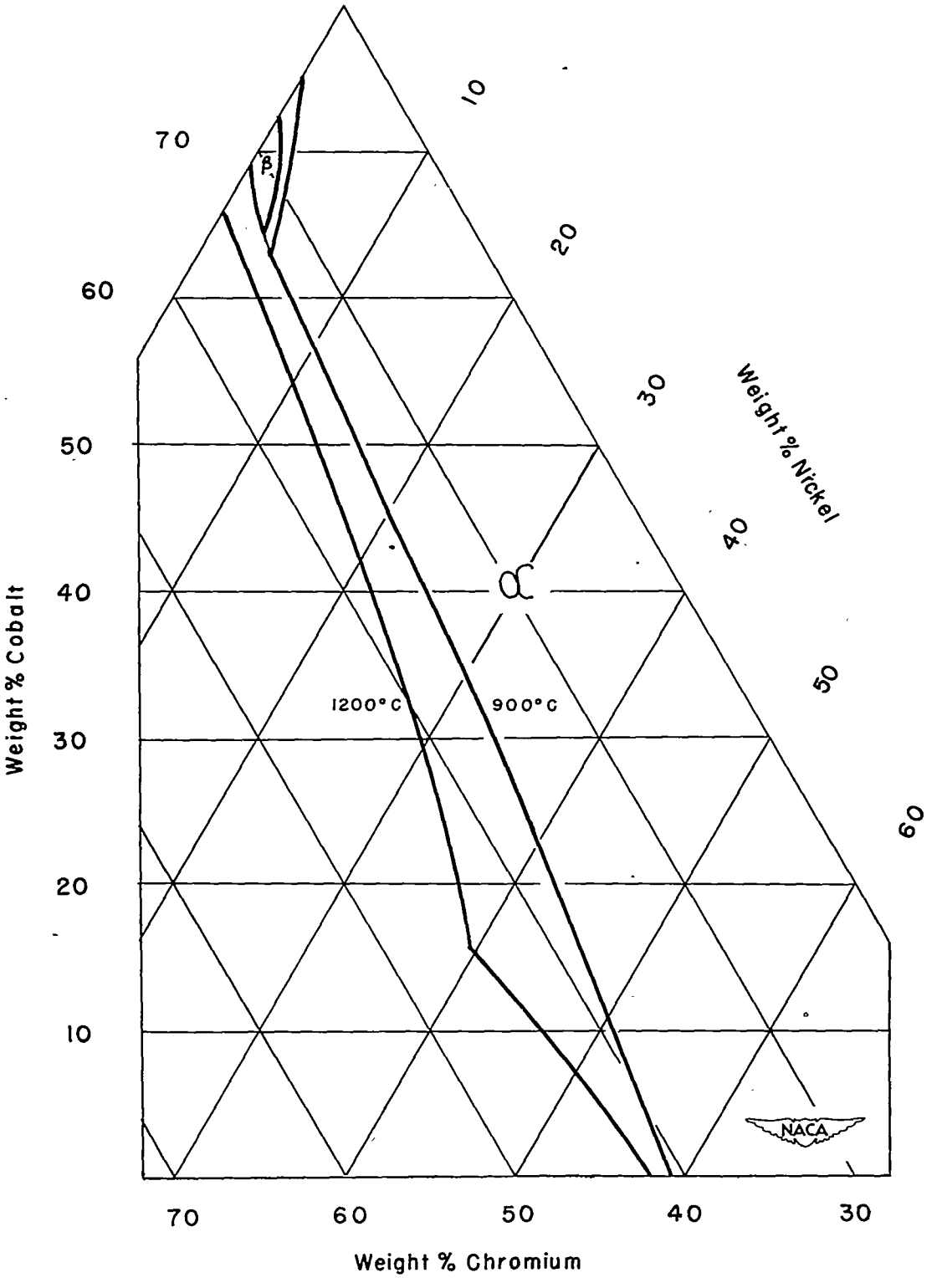

Figure 18.- Alpha phase boundaries at 900° C and 1200° C in cobalt-chromium-nickel system and beta phase boundaries at 900° C.

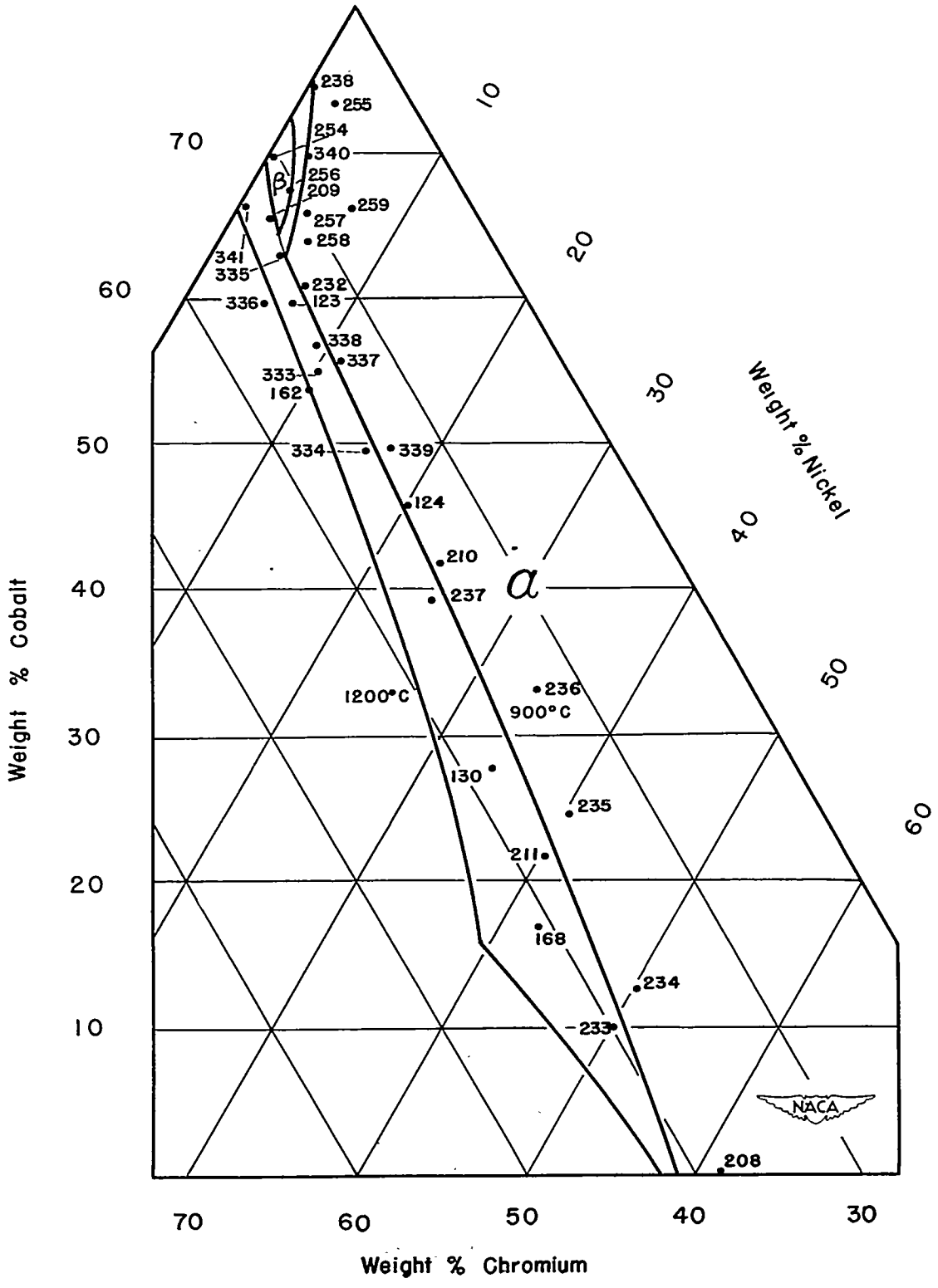

Figure 19.- Alpha phase boundaries at 900° C and 1200° C in cobalt-chromium-nickel system and beta phase boundaries at 900° C with chemical composition of alloys (see table VII).

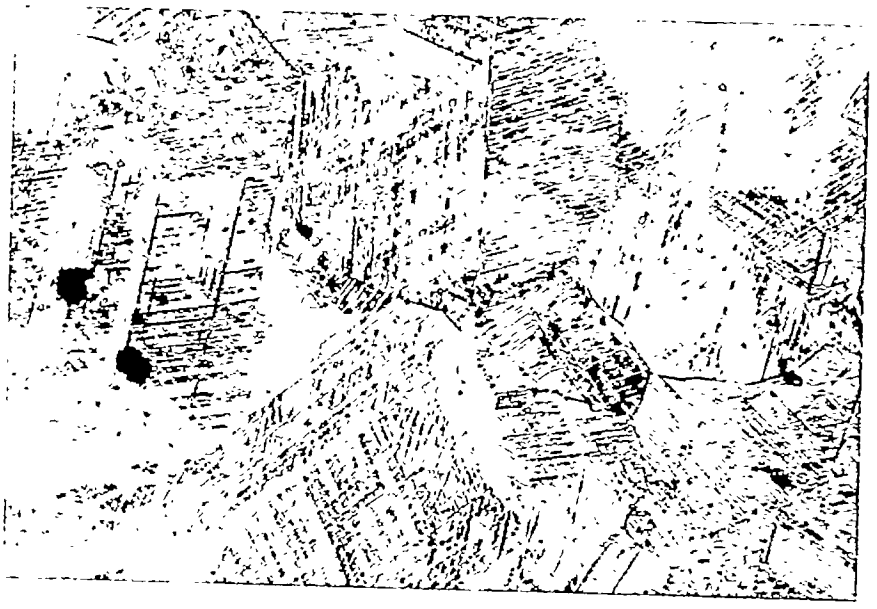

Figure 20.- Alloy 258 containing 63.95 percent cobalt, 30.98 percent chromium, and 5.07 percent nickel. Electrolytically polished and etched with reagent 1; transformed structure of an alloy in alpha phase field of cobalt-chromium-nickel system quenched from 900° C to room temperature; X400.

Figure 21.- Alloy 254 containing 70 percent cobalt and 30 percent chromium. Electrolytically polished and etched with reagent 1; quenched from beta phase field at 900° C to room temperature; Widmanstätten precipitate is probably a sigma-phase precipitate formed on cooling; X400.

Figure 22.- Alloy 238 containing 74.70 percent cobalt and 25.20 percent chromium. Electrolytically polished and etched with reagent 1; beta-phase particles in alpha-phase matrix marked by transformation striations which develop upon quenching from 900° C to room temperature; X400.

Figure 23.- Alloy 233 containing 10 percent cobalt, 40 percent chromium, and 50 percent nickel. Electrolytically polished; typical distribution of second-phase particles in alloy whose composition located alpha phase boundary; X750.

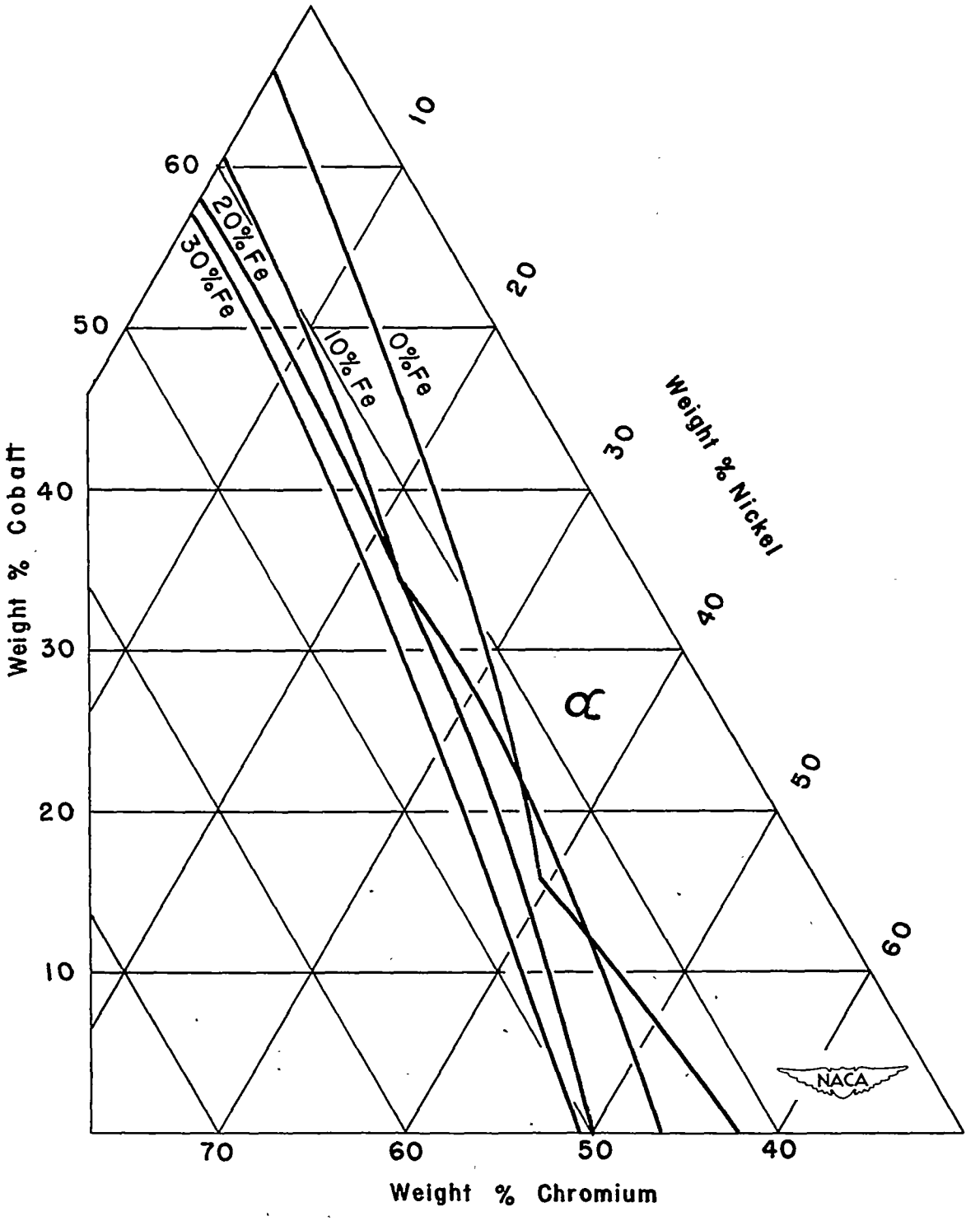

Figure 24.- Alpha phase boundaries in cobalt-chromium-iron-nickel system at 1200° C at iron contents of 0, 10, 20, and 30 percent.

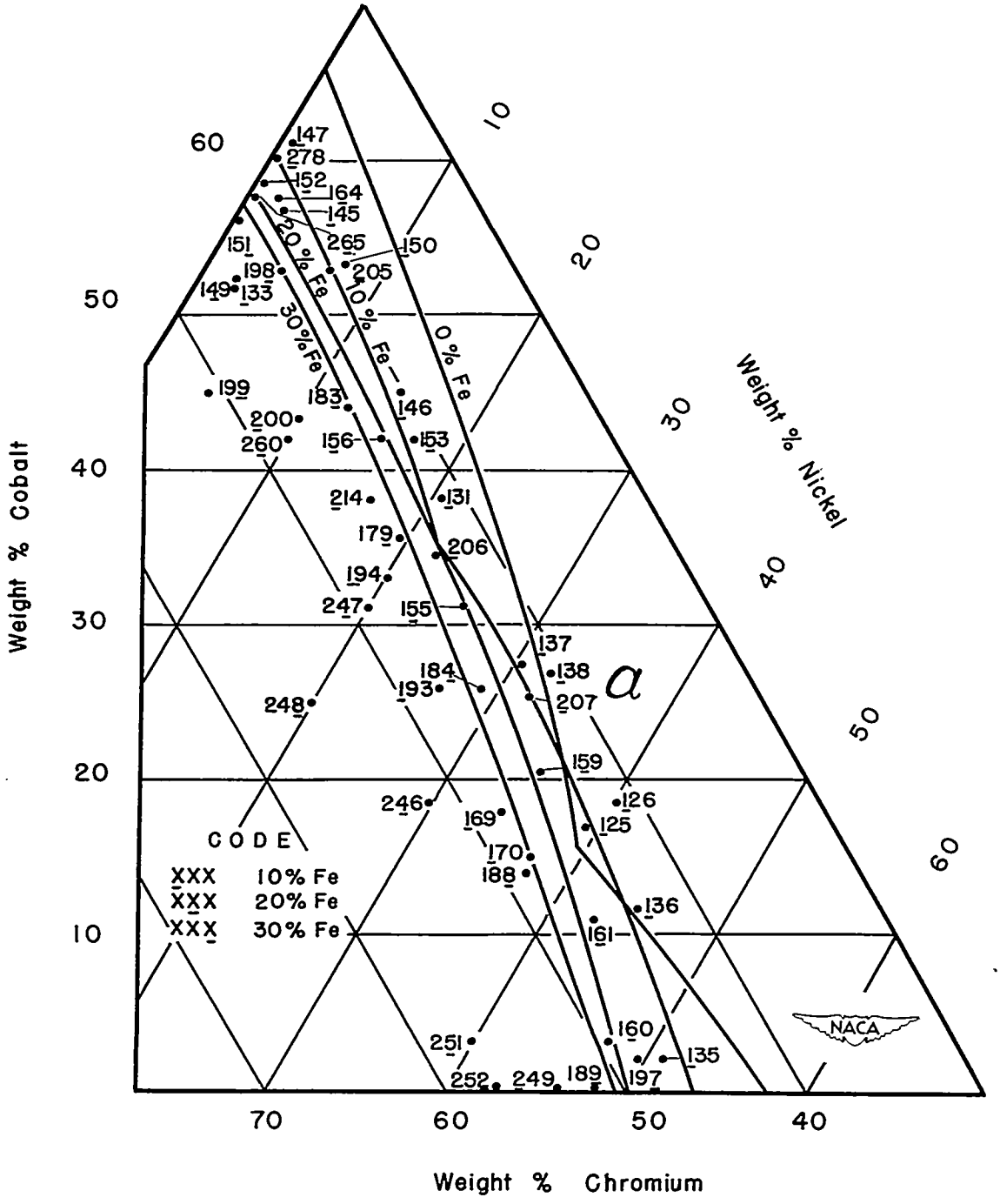

Figure 25.- Alpha phase boundaries in cobalt-chromium-iron-nickel system at 1200° C at iron contents of 0, 10, 20, and 30 percent together with alloy compositions as given in table IX.

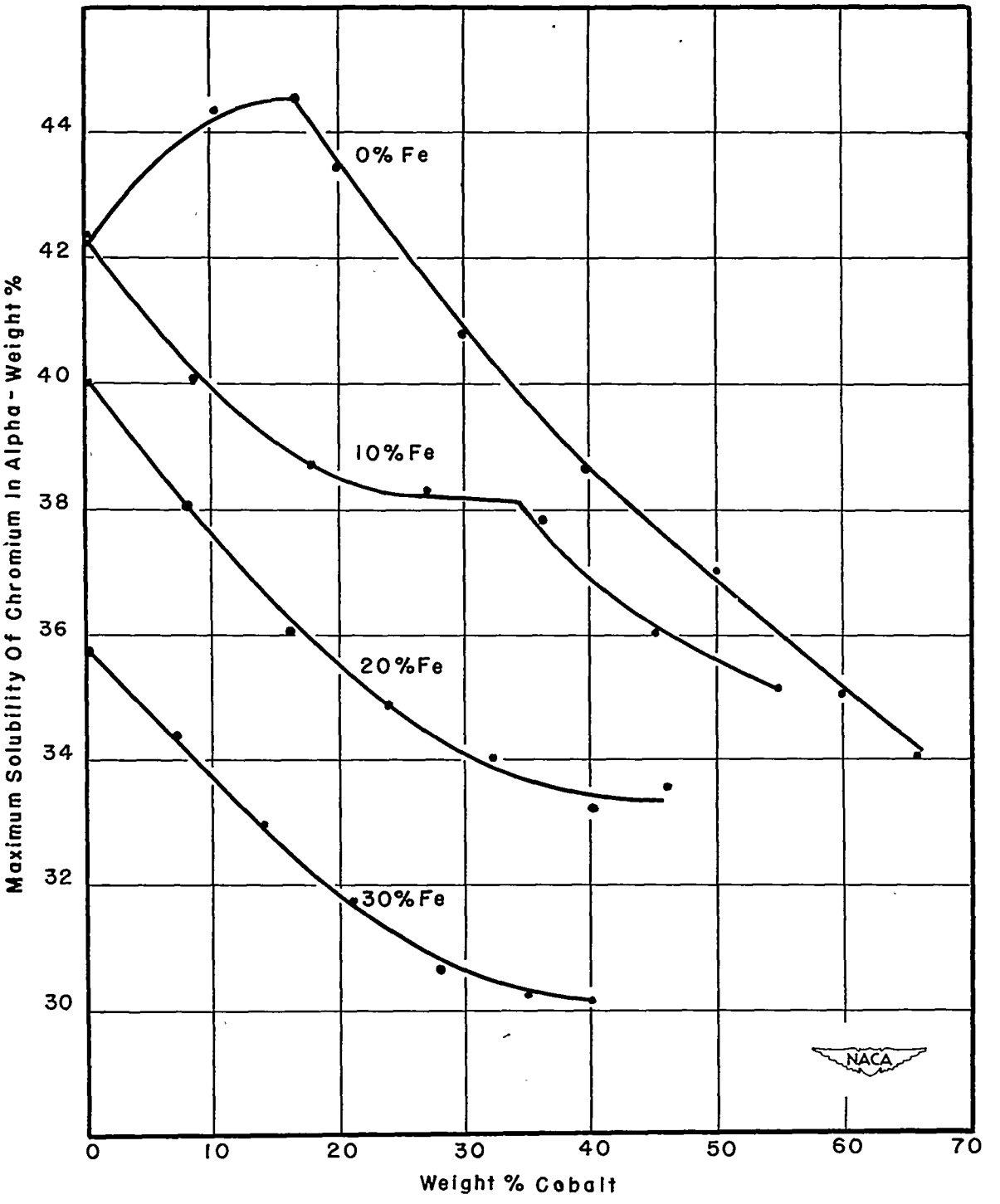

Figure 26.- Maximum solubility at 1200° C of chromium in alpha phase of cobalt-chromium-iron-nickel alloys plotted as function of cobalt content for iron contents of 0, 10, 20, and 30 percent. Data in table X.

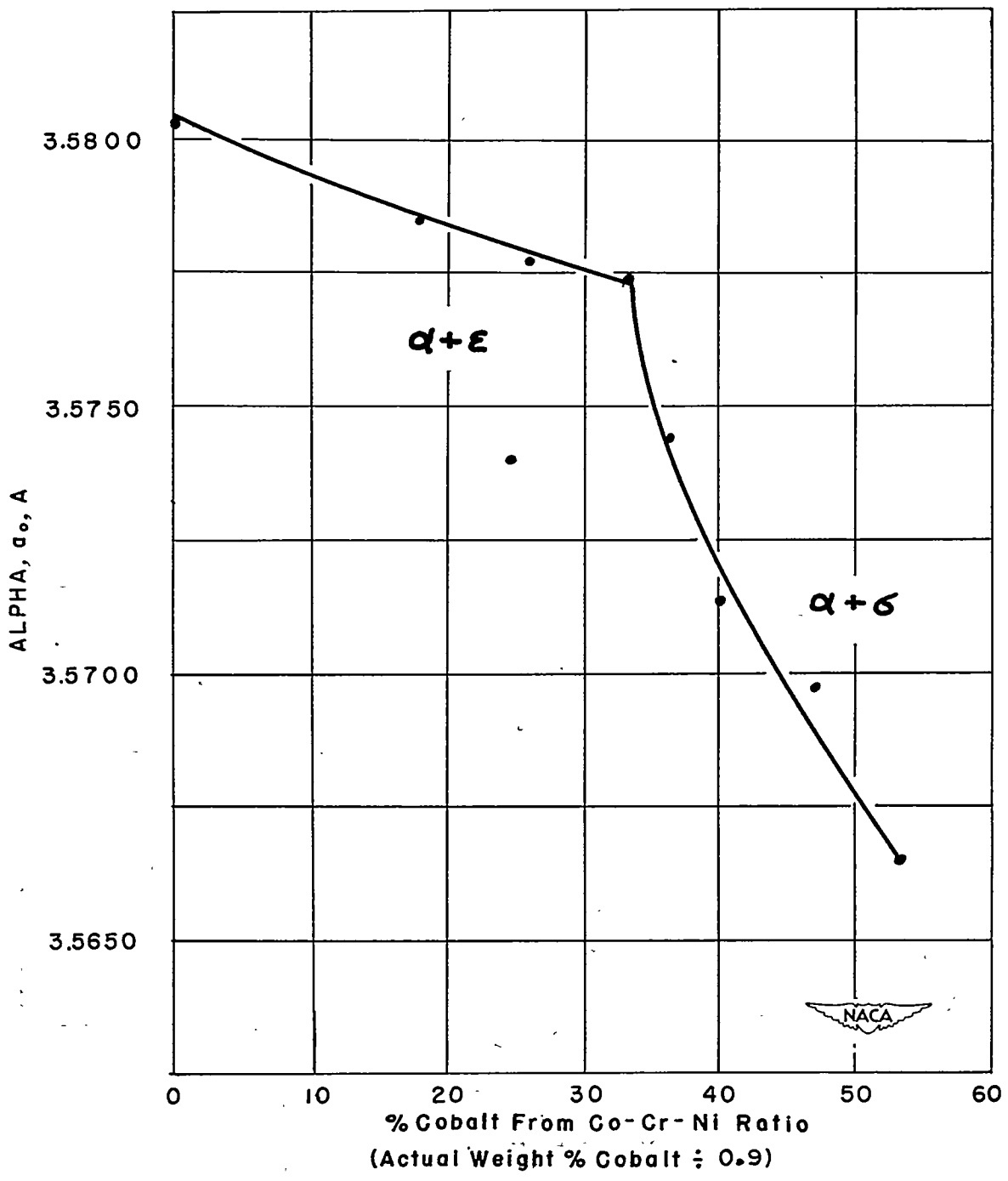

Figure 27.- Variation of lattice parameter of 1200° C alpha-phase-boundary alloys containing 10 percent iron in cobalt-chromium-iron-nickel system plotted as function of corrected cobalt composition. Data in table XI.

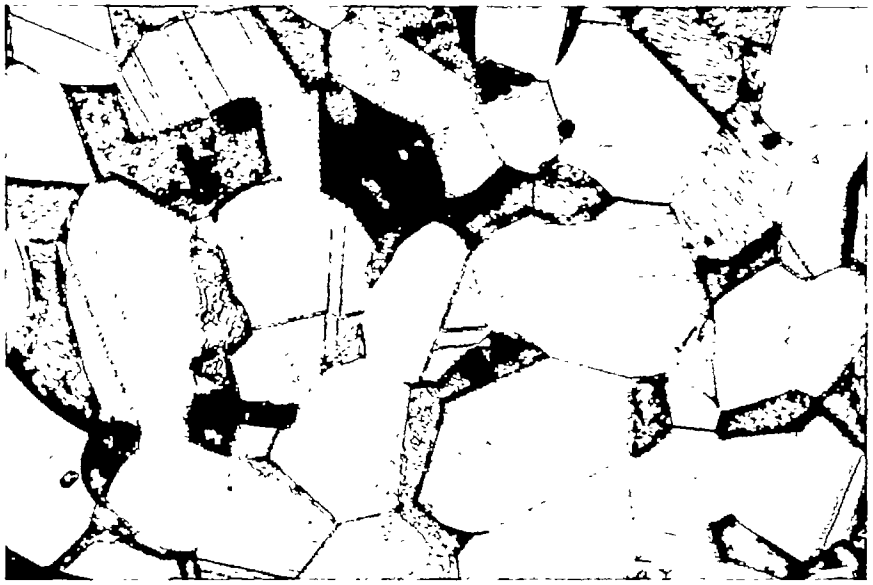

Figure 28.- Alloy 199 containing 31.5 percent cobalt, 35.7 percent chromium, 30 percent iron, and 2.8 percent nickel. Electrolytically polished and deeply etched with reagent 1; epsilon phase more heavily etched than alpha-phase matrix; X200.

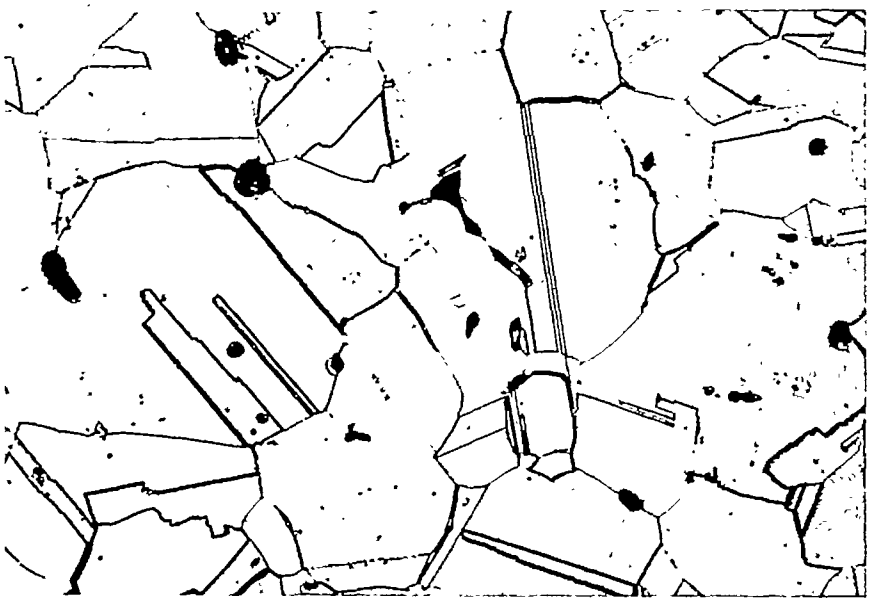

Figure 29.- Alloy 207 containing 20.7 percent cobalt, 40.5 percent chromium, 10 percent iron, and 28.8 percent nickel. Electrolytically polished and etched with reagent 1; alpha-phase matrix with second phase etched away; X200.

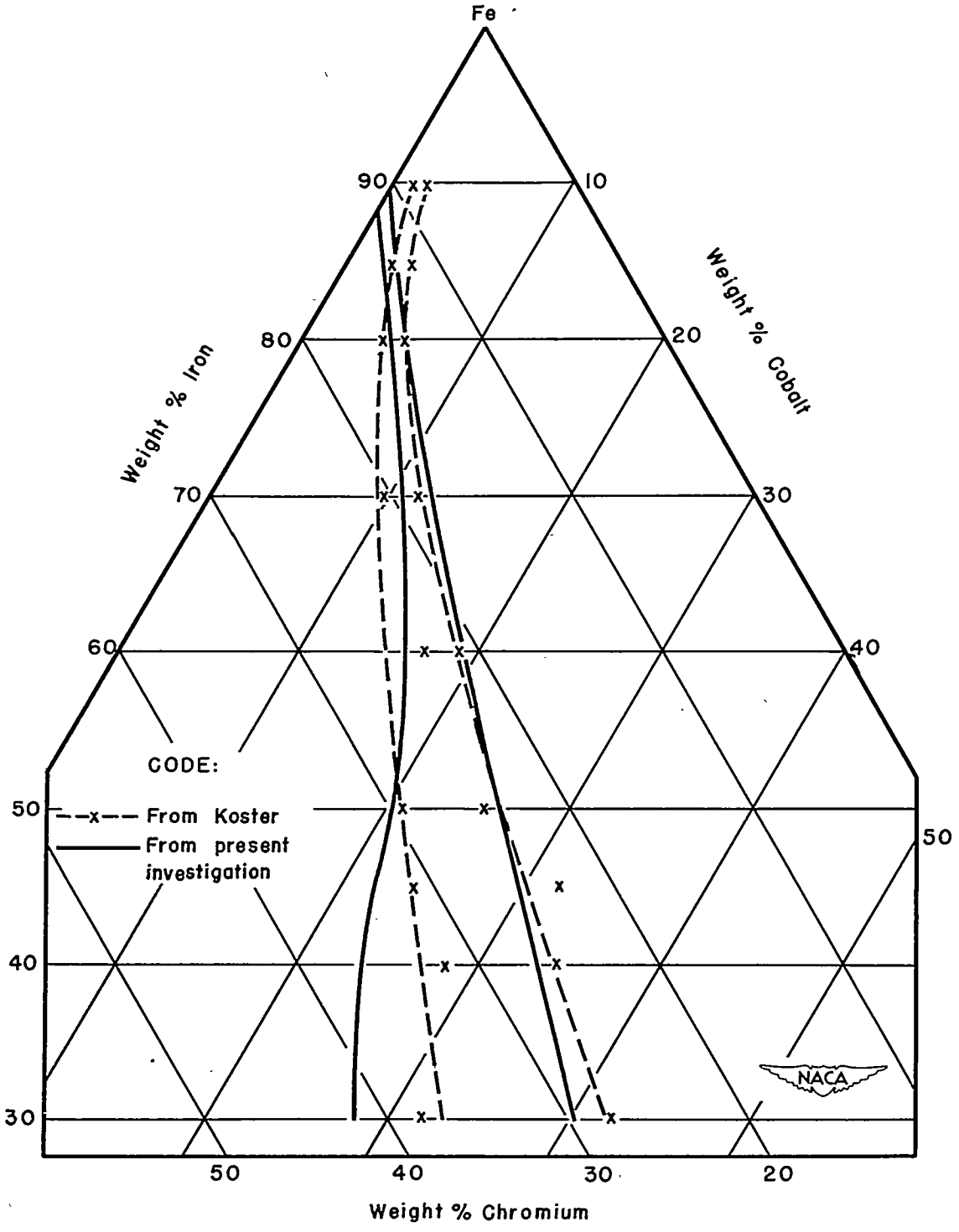

Figure 30.- Boundaries of alpha and epsilon phases in cobalt-chromium-iron system at 1200° C for alloys containing more than 30 percent iron, plotted from data in table XIII (Koster) and from data in table III (present investigation).

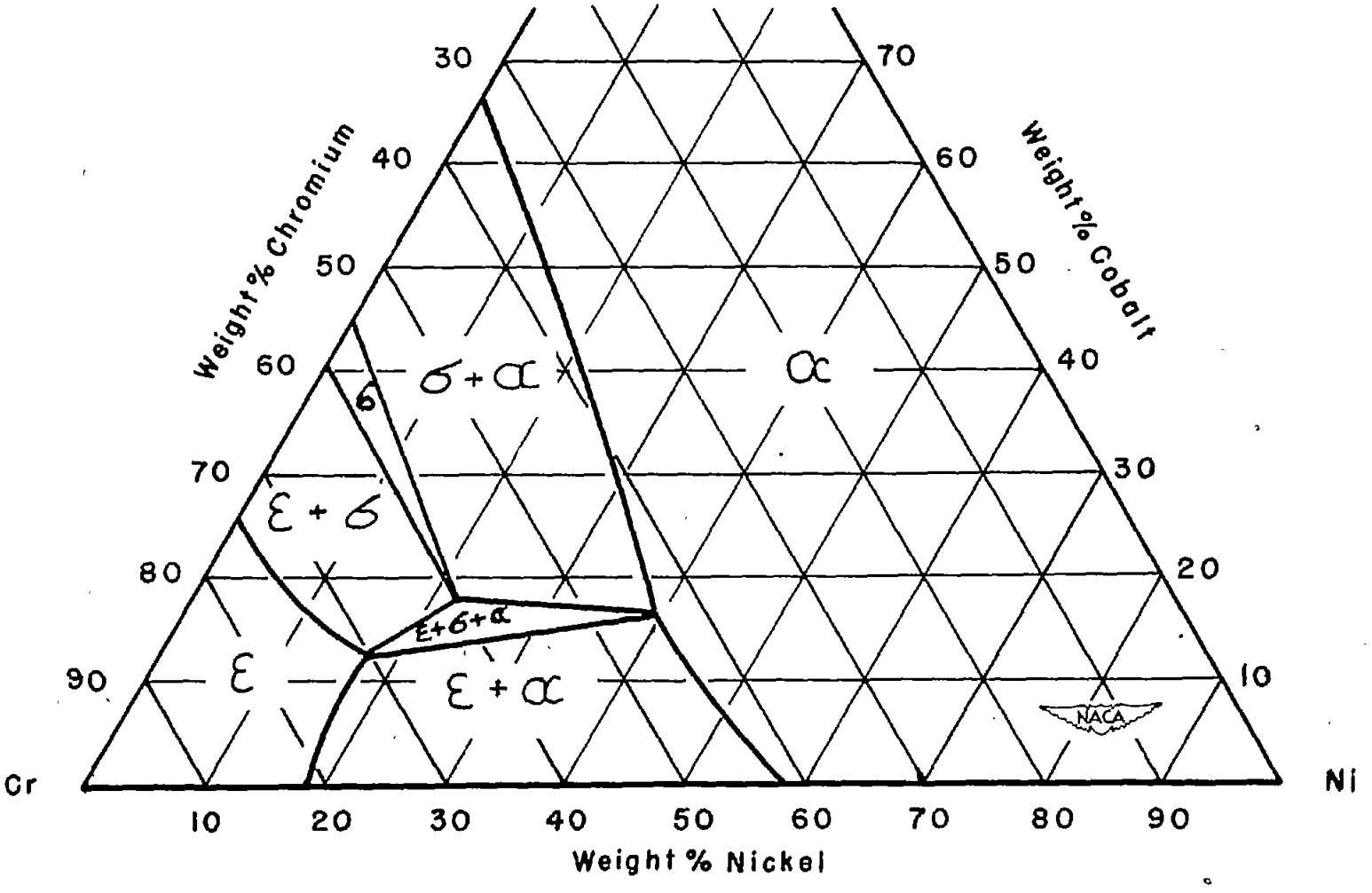

Figure 31.- Revised phase diagram of cobalt-chromium-nickel system at 1200° C.

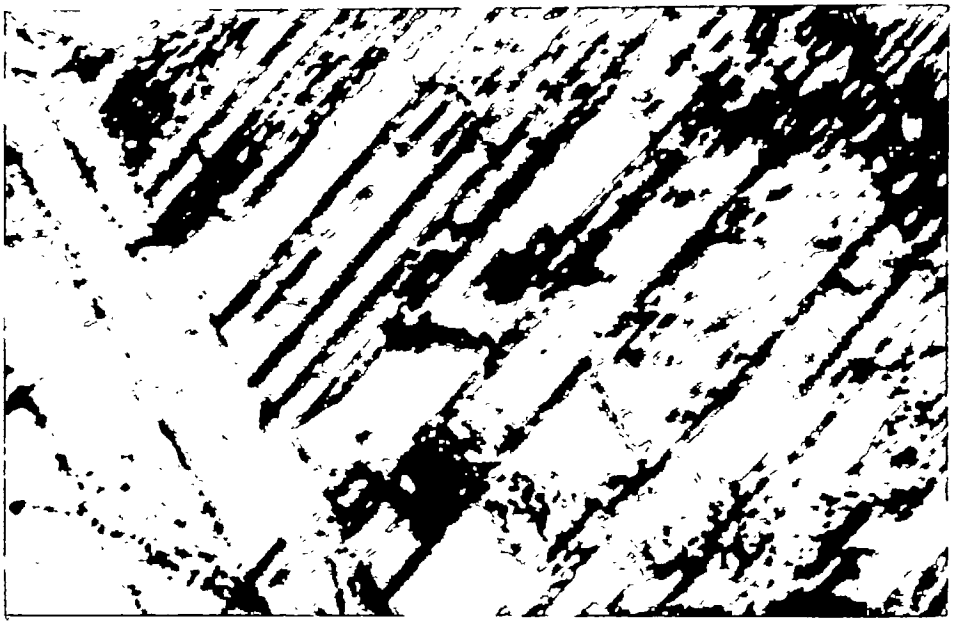

Figure 32.- Alloy 104 containing 65.4 percent cobalt and 34.6 percent chromium. Electrolytically polished and etched with reagent 1; striations in structure of partially transformed alloy of area B, figure 1; X2500.

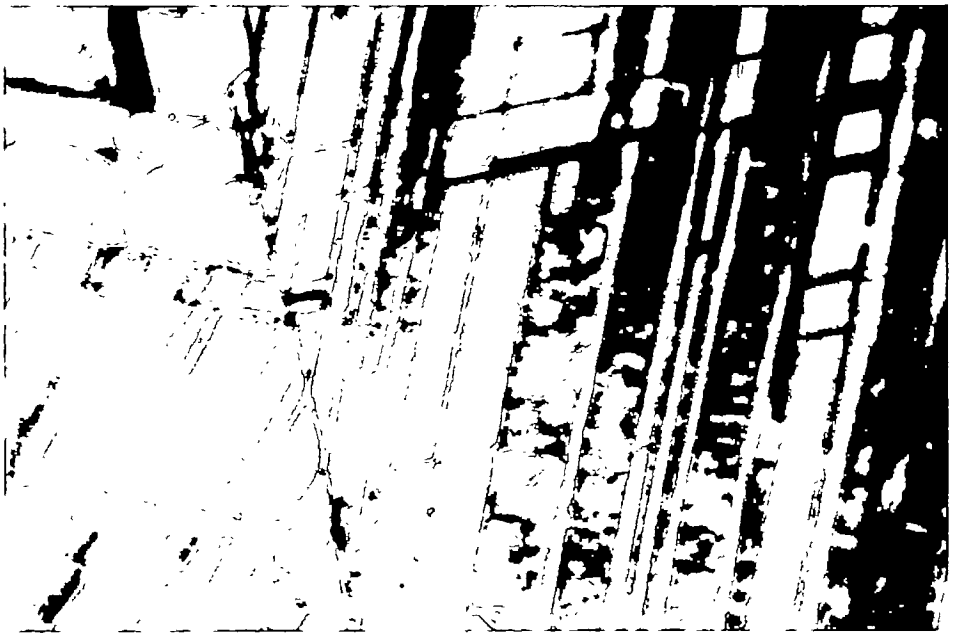

Figure 33.- Alloy 201 containing 61.63 percent iron, 18.94 percent cobalt, and 19.42 percent chromium. Electrolytically polished and etched with reagent 1; striations in structure of partially transformed alloy of area B, figure 1; X2500.

NACA-Langley - 3-4-52 - 200