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By W. D. Manly and Paul A. Beck

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SURVEY OF THE CHROMIUM-COBALT-NICKEL PHASE DIAGRAM AT 1200° C

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SUMMARY

A survey of the chromium-cobalt-nickel ternary phase diagram at 1200° C was made by means of microscopic and X-ray diffraction studies on 110 vacuum-melted alloys prepared from commercial metals of the highest purity available. At 1200° C the following phases occur: (1) Very extensive face-centered cubic solid solutions, based on the binary cobalt-nickel solid solutions; (2) body-centered cubic chromium-base solid solutions; and (3) brittle sigma solid solutions, based on the chromium-cobalt sigma phase which is isomorphous with the iron-chromium sigma phase. In the sigma solid solutions well over half of the cobalt can be replaced by nickel with relatively little change in the chromium content. The diagram indicates that the sigma phase may coexist with alpha of a nickel-cobalt ratio higher than 2. The brittleness of alloys consisting essentially of the body-centered cubic phase is correlated with the platelike precipitate of sigma in these alloys.

INTRODUCTION

A great number of commercial alloys have been developed in recent years for high-stress service at high temperatures. Most of these alloys contain at least five or six components. With alloys of that complexity it is very difficult to establish the optimum composition range merely on an empirical basis without using the correlation between structure and properties as a guiding principle. In order to make use of this correlation, some knowledge of the phase diagrams concerned is necessary.

The determination of phase diagrams for systems of five or six components is an extremely laborious procedure. It would obviously have to start with establishing the phase relationships in systems of a lesser number of components, such as two or three. The work could then continue by adding one new element at a time; without such a systematic approach one would quickly get lost in unknown territory.

In order to expedite the obtainment of useful results, it was decided to restrain the general survey to a single temperature. The temperature 1200° C was chosen because it lies in the temperature range where most of the commercial alloys are solution-treated and the results are, therefore, of immediate practical interest. Another reason for selecting this temperature was that it allows diffusion to proceed fast enough so that equilibrium could be approached in reasonable annealing periods. It was realized that the phase relationships at lower temperatures such as the range of 720° to 870° C are of equal, if not more, practical interest, since this is the actual operating temperature range for such alloys. However, the annealing times required to approach equilibrium at lower temperatures are so long for most of these alloys that the use of this temperature range for general survey work, where a large number of specimens have to be heat-treated and studied, would have been quite impractical.

Therefore, the approach decided upon in this work was first to complete the 1200° C isothermal survey starting with the chromium-cobalt-nickel ternary system and continuing with quaternary systems to study the effects of additional elements, such as iron, molybdenum, tungsten, and carbon. It was also planned to extend the work toward lower temperatures in certain critical composition ranges which are of immediate practical importance.

The results given in the present report constitute the first part of this program and comprise data for the isothermal section at 1200° C of the chromium-cobalt-nickel system.

The nomenclature adopted in this report conforms to that used by Elsea, Westerman, and Manning (reference 1) for the cobalt-chromium binary system, since at 1200° C the phases occurring in the ternary system are all based on the binary cobalt-chromium phases. An exception is the intermediate phase, which was designated by those authors as gamma. Since this phase recently turned out to be isomorphous with the iron-chromium sigma phase and may be expected to form extended solid solutions with the latter, the more generally known designation "sigma phase" was adopted for it.

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The authors wish to express their gratitude to Mr. J. D. Nisbet of the General Electric Co. for contributing a series of chromium-cobalt-nickel alloys and to Mr. H. C. Cross and Mr. A. R. Elsea of Battelle Memorial Institute for helpful discussions. Mr. Hengtie Lee, University of Pennsylvania, collaborated in the early stages of the work.

LITERATURE SURVEY

A thorough search of the existing literature pertaining to the chromium-cobalt-nickel ternary system was made but no published data were found. The three adjoining binary systems had been investigated by previous workers. The best data found in the existing literature are reviewed in the following.

The diagram of the cobalt-nickel binary system, as given by Hansen in reference 2, features a complete series of solid solutions. The chromium-nickel diagram of Jenkins, Bucknall, Austin, and Mellor in reference 3 represents the most recent work (1937) on this system. It gives the solubility limit at 1200° C of the chromium-rich solid solution at 16 percent nickel and of the nickel-rich solid solution at 55 percent nickel. The chromium-cobalt binary diagram was clarified by Elsea, Westerman, and Manning's paper of 1948 (reference 1). According to these authors at 1200° C the cobalt-rich solid solution extends to 36 percent chromium and the chromium-rich solid solution begins at 69 percent chromium. The composition range of the brittle intermetallic compound gamma is between 53 percent and 58 percent chromium.

It was recently shown by Sully and Heal (reference 4) that the gamma phase of the chromium-cobalt system and the sigma phase of the iron-chromium system are isomorphous.

Since the work at this laboratory is being extended to the quaternary iron-chromium-cobalt-nickel system, it was felt desirable to avoid introducing two different designations for the isomorphous end members of what may be expected to be a continuous series of solid solutions. For this reason, and because the designation "sigma" is more familiar to metallurgists, it was decided to use that designation in the chromium-cobalt-nickel ternary diagram for the brittle phase previously known in the chromium-cobalt binary system as the gamma phase.

Whether or not the ternary system comprises additional phases, not present in the three binary diagrams, was unknown at the outset, since no information could be found relating to this system.

EXPERIMENTAL PROCEDURE

The disappearing phase method was used throughout this work. A study of the X-ray diffraction pattern and of at least one metallographic specimen was made for each of the 110 alloys prepared. In all cases the X-ray analysis and the microscopic examination were

used in conjunction to identify the phases. For each alloy at least one chemical analysis was made and numerous alloys were analyzed spectrographically for a check on the impurities present. In some cases chemical-analysis specimens were taken both from the top and from the bottom to check the degree of segregation in the casting.

A series of ternary chromium-cobalt-nickel alloys, placed systematically every 10 percent throughout the diagram, were made by Mr. J. D. Nisbet of the General Electric Co. at Schenectady. Samples from each of the alloys were run through the same procedure - homogenizing treatment, metallographic examination, and so forth - that was followed on the alloys originating at Notre Dame.

The following description gives the details of the methods of melting, homogenizing, metallographic work, and X-ray analysis used.

Starting Materials

The materials used in this investigation were commercial electrolytic chromium, electrolytic nickel, and cobalt rondelles; a lot analysis of each is given in table 1.

Melting

The melting techniques employed varied a great deal as the work progressed. However, all the alloys were melted in the same vacuum induction furnace and were allowed to solidify in vacuum. The two main problems encountered in melting the alloys were to avoid the formation of bridges in the melting crucible near the top of the charge and to reduce the chromium-oxide content. To solve the first problem an electrically conducting sleeve was used around the melting crucible, in which much of the heat was generated. Two types of sleeve were used, graphite and molybdenum. It was attempted to reduce the chromium oxide by making additions of graphite powder to the charge and by almost completely surrounding the melting crucible with a graphite crucible and cover.

Alloys 1 to 25 were melted without a sleeve; considerable difficulty was encountered as the top of the charge bridged over and the melt had to be greatly overheated to liquefy this bridge. From alloy 26 on, the alloys were melted by using a heating sleeve. In melts 25 to 31 a graphite sleeve was used with good results. A molybdenum sleeve was used with melts 32 to 36, but even at the lowest power setting for the Ajax converter this sleeve caused the charge to overheat. Therefore, from alloy 37 on the arrangement in figure 1 was used, in

which the refractory crucible (3) was placed inside a graphite crucible (2) and the graphite crucible with its cover (4) was enclosed in a silica brick insulating sleeve (1).

Three different types of refractory crucibles were tried - zirconia, stabilized zirconia, and magnesia. The magnesia crucibles were used for alloys 9, 10, 11, 12, 15, and 17 but were not satisfactory, as there was considerable reaction with the melt and resulting magnesium pickup in the alloy. The stabilized zirconia crucibles, strangely, cracked, thus losing the charge (they were tried three times with the same results). The zirconia crucible was by far the best, although even here there was some reaction with the melt. A more detailed description of this will be given later. The zirconia crucibles used were Nos. 10 and 14, manufactured by the Titanium Alloy Manufacturing Co., No. 10 making a 100-gram melt and No. 14 making a 300-gram melt.

Early in the work the microscopic examination showed considerable amounts of chromium oxide; to improve this a carbon addition for deoxidizing the melt seemed in order. From melt 9 to melt 14 carbon was added in the form of graphite powder with the assumption that the cobalt contained 0.5 percent oxygen (O_2), thus adding 0.0018 gram carbon per gram of cobalt. This did not solve the problem so the graphite addition was correlated with the amount of chromium; the carbon addition was varied from 0.0007 gram carbon per gram of chromium to 0.0027 gram carbon per gram of chromium. This was done in melts 14 to 36. Both of these attempts were essentially unsuccessful. From melt 37 to the completion of the work, a graphite cover with a viewing hole of 1/4-inch diameter was placed on top of the graphite crucible surrounding the refractory crucible. This helped in two ways; the entire melting crucible was enclosed in graphite providing a reducing atmosphere, and the cover kept any stray silica particles from the insulating sleeve out of the melt. Both chemical analysis and microscopic examination showed that this was by far the most effective means of keeping the oxide content low in the castings.

The preceding paragraphs point out the changes in melting techniques as the work progressed. The following discussion will outline the various steps taken in every melt that was made.

The charge was placed in the crucible in the following order: Chromium at the bottom, cobalt in the middle, and nickel at the top. This order was maintained so the lowest melting constituent would always be on top. The melting crucible, surrounded by the graphite crucible and the silica sleeve, was enclosed in the Vycor tube of the high-frequency induction melting furnace (fig. 2). The mechanical pump was turned on and when the vacuum was 30 microns of mercury or better, the entire system was flushed with dried medical helium in the following manner (see figs. 3 and 4): (1) Close valve 1; this shuts

the mechanical pump out of the system; (2) open valve 3 and introduce medical helium until the system has just balanced the atmospheric pressure as seen on the manometer; (3) close valve 3; (4) open valve 1, thus bringing the mechanical pump back into the system. (Note: Valve 2 is there as a safety precaution to cut the manometer out of the system when the mechanical pump is again connected with the system, after flushing with helium.)

After the charge had been flushed three times as explained, the power was turned on at the lowest setting possible with the Ajax converter used, approximately 5 kilowatts. When the charge reached a red heat it was flushed with dried medical helium three more times. After the third helium flush at red heat, the power was increased until the charge melted. As soon as the charge melted, it was given a final helium flush before the power was decreased so that the charge would just stay molten. The charge was held molten until the vacuum was approximately 50 microns or the charge had been molten for 30 minutes. Temperature readings were made with a Leeds and Northrup filament-type optical pyrometer and during the "holding-molten" stage temperature and pressure readings were taken simultaneously. At the end of the "holding-molten" stage the power was turned off and the melt was allowed to solidify in the crucible in vacuum.

Upon removal from the crucible the ingot was cut into several pieces which were numbered from top to bottom. The top piece (1) was used for chemical analysis, the next piece (2) was used for studying the as-cast microstructure, and the next (3), for microscopic and X-ray diffraction work after the homogenizing treatment. In several cases the extreme bottom piece was also used for chemical analysis. The remainder of the casting was used for further homogenizing treatment and for checking chemical analysis, microstructures, and so forth.

Homogenizing Treatment

The homogenizing treatment was done in a platinum resistance vertical tube furnace. At first the protective atmosphere used in this furnace was medical helium which had been passed over copper turnings at 450° C and through "Drierite" drying columns before entering the furnace. Finally, after trying several variations and additions, the following protective atmosphere was adopted. A mixture of 92 percent helium and 8 percent hydrogen was passed through "Deoxo" catalyst, copper turnings at 300° C, "Drierite" drying column, Pittsburg Lectrodryer (activated alumina), and calcium hydride, in the order listed, before entering the furnace tube. Two homogenizing furnaces were used and so arranged that gas could be supplied to them either separately or together (fig. 5).

Considerable care was exercised in using the furnaces; the setting of the needle valve for correct flow of gas and the proper seating of the rubber stopper at the ends of the sillimanite tube were quite critical. Another precaution taken at the time of charging was to flush the furnace tube before lowering the sample into the hot zone. Also, it was found necessary to water-cool the top rubber stopper. In order to avoid the back diffusion of water vapor into the furnace tube from the flow bottle, it was found necessary to use a "Drierite" tube between the flow bottle and furnace tube or substitue vacuum-pump oil for water in the flow bottle.

The homogenizing period used was 12 or 75 hours at 1200° C. The samples were suspended into the hot zone of the furnace on Nichrome wire. At the end of the homogenizing period the samples were water-quenched by dropping them into the quenching bath directly through the bottom opening of the tube, with the stopper momentarily removed.

All the alloys around the epsilon and sigma phase boundaries were homogenized for 75 hours and water-quenched. Whenever the microscopic examination, X-ray analysis, and chemical analysis did not agree, the alloy in question was homogenized for 75 hours. Coring was seen in the alpha-plus-epsilon alloys and in some of the epsilon-plus-sigma alloys. Whenever coring still existed after the 12-hour homogenizing treatment, the alloys were given the 75-hour homogenizing treatment.

The alpha boundary alloys were so ductile that forging was feasible. A crude but effective forge was used, consisting of an anvil and sledge hammer. The specimens were heated at 1200° C for 25 minutes and then hot-forged. This forging operation easily gave 50-percent reduction of thickness. After forging, the alloys near the alpha boundary were subjected to a 75-hour 1200° C homogenizing treatment, followed by a water quench. Alloys containing appreciable amounts of the sigma phase or of the epsilon phase could not be forged.

Metallographic Technique

From each ingot at least two samples were prepared for microscopic examination, one for the as-cast structure and the other for the homogenized structure. The as-cast microscopic examination was used mainly as a check on the oxide content of the casting. The surface polished was the one closest to the top of the original casting, since the chromium oxide was found to concentrate at the top of each melt. Approximately 1/8 to 1/4 inch of stock was ground from the homogenized specimen to remove any possible trace of nitride or oxide from the surface to be polished. The samples were polished by the conventional

metallographic methods, finishing with a two-wheel lapping operation on billiard cloth, using Linde gamma alumina as the abrasive.

After trying numerous etching reagents, the following reagents were used throughout the work.

Reagent 1 - Alkaline permanganate.- The specimen was etched electrolytically for 10 to 30 seconds in a 2-percent sodium-dichromate solution with a current of 400 milliamperes. The specimen was then washed in distilled water and dipped for 15 to 20 seconds into a solution consisting of equal parts of 15-percent potassium-permanganate solution and 8-percent sodium-hydroxide solution.

Reagent 2.- The specimen was dipped into a saturated cupric-chloride hydrochloric-acid solution for 30 seconds. This was used mainly for macroscopic etching.

Reagent 3.- This reagent contained: 10 cubic centimeters nitric acid, 20 cubic centimeters hydrochloric acid, 20 cubic centimeters glycerol, and 10 cubic centimeters hydrogen peroxide 3-percent concentration. The specimens were dipped into the solution for 30 seconds. Hydrogen peroxide was the most critical constituent of the reagent.

The alpha phase which covers more than half of the 1200° C section is a face-centered cubic structure corresponding to nickel and to the high-temperature modification of cobalt. With reagents 2 and 3 the alpha phase did not stain at all, but with reagent 1 it was stained yellow to light brown depending on the etching time. None of the etchants would bring out the grain boundaries satisfactorily in the alpha phase.

The epsilon phase is the chromium-rich solid solution having a body-centered cubic lattice. Reagent 1 stained it a light yellow and brought out the grain boundaries quite plainly. In cases where the specimen was largely epsilon better results were obtained by electrolytically etching with the 2-percent sodium-dichromate solution but omitting the staining with the alkaline permanganate solution. Reagent 3 darkened the epsilon slightly. Almost all epsilon samples showed a precipitate that will be discussed in more detail later (figs. 6 and 7).

The sigma phase, whose complex crystal structure is still unknown, is a brittle intermetallic compound. Reagent 3 darkens the sigma phase to a color varying from light brown to purple, depending on the etching

time. Frequently, positive identification of sigma was made by observing the cracks running through it and stopping at the epsilon and alpha phases (figs. 8 and 9).

During the actual work the above etchants had to be varied considerably in determining the exact identity of a small amount of a phase. Differentiating between a small amount of the sigma phase or of the epsilon phase in a matrix of alpha was difficult. It was found that etching the specimens electrolytically with the sodium-dichromate solution causes the small sigma particles to turn light brown, while small epsilon particles did not stain.

The alpha-plus-epsilon alloys were very hard to etch. For these alloys reagent 3 was found useful. The electrolytic sodium-dichromate etch, without the alkaline permanganate stain, could also be used; however, the etching time was quite critical (figs. 10 and 11).

The alpha-plus-sigma and the epsilon-plus-sigma alloys were always easy to differentiate by means of reagent 1. The sigma phase always etched from light brown to purple, while alpha and epsilon stayed white or etched a light yellow. The alpha and epsilon particles in these two-phase regions were recognized since the epsilon usually showed a precipitate and its grain boundaries were always outlined, while alpha did not show grain boundaries (figs. 8, 9, 12, and 13).

The estimation of the amounts of phases present was done by observing the microstructure and assigning relative values to the amounts of phases present. This method depended wholly on the judgment of the operator and when there were large primary particles of one phase surrounded by small particles of both phases, it was a very delicate job. In comparing the amounts of phases expected from the diagram against the amounts of phases found in the microscopic examination it was gratifying to see the agreement. It might be mentioned that the estimation of the amounts of phases was done before the chemical analyses were obtained, so the observer could not be swayed by previous knowledge of the amounts of phases expected.

X-Ray Analysis

In this investigation an unsymmetrical focusing camera designed by Mr. E. R. Jette was used. The camera was calibrated with pure lead and sodium chloride; from this calibration the true slit-to-knife-edge distance and the radius of the camera were calculated. The range covered by the camera is from 18.6° to 78.4° and the slit-knife-edge distance was found to be 13.13 centimeters. This value of 13.13 centimeters was used in all measurements made on patterns taken with the unsymmetrical focusing camera.

The powders were prepared from a homogenized portion of each alloy by filing or with a percussion mortar depending upon the brittleness of the sample. The powders were sealed in an evacuated fused-quartz capsule and then heat-treated for 1 hour at 1200° C followed by a water quench. After examining the powders for any sign of contamination, an X-ray specimen was prepared by gluing the powders on a card with airplane cement. The X-ray diffraction patterns were taken by using unfiltered chromium radiation from a hot-cathode-type tube operating at 38 kilovolts and 8 millamperes, using a 1-hour exposure.

During the course of the investigation it was found that in some cases the 1-hour stress-relieving period was too long for the powders, as they sintered together, so the annealing time was cut to 30 minutes. This was especially true in powders from alpha-plus-sigma alloys. The annealed powders would not give a sigma diffraction pattern while powders from the same alloy not annealed gave a sharp sigma pattern. (The sigma lines did not show broadening due to cold-work, probably because of the brittleness of the sigma phase.) Whenever the microscopic examination showed considerable amounts of the sigma phase but the X-ray pattern was devoid of sigma lines a pattern was taken on a new sample prepared with the powder in the unannealed state. (See section "Experimental Results" and table 2.)

Standard patterns for all known phases of the system were prepared as they were used to solve the pattern of each of the alloys. Typical patterns of the three phases of this system are given in tables 3 to 5.

Diffraction patterns were made of the two-phase specimens from the forged and 75-hour-homogenized alloys near the alpha boundary, the positions of 4 lines of each pattern were measured 10 times each, and the average distance for each line was computed. These average values were used in order to improve the accuracy in the calculation of a_o, since the lines of the patterns were rather broad. To help eliminate the systematic errors, the final a_o was obtained by plotting a_o against $\cos^2\theta$ and extrapolating to a value of θ of 90°. From various epsilon-plus-sigma and alpha-plus-sigma diffraction patterns the d values were calculated to determine the change in d values with the nickel content. All measurements were made from the high-angle knife edge to the twenty-seventh line of the sigma pattern. Therefore, the greatest distance measured was less than 3 centimeters, so that the film-shrinkage error was negligible.

Microhardness

All the alpha boundary alloys were tested with a Tukon Hardness Tester to find the correlation between the hardness of the alpha phase

and cobalt content. In determining the hardness of the alpha phase in each alloy five indentations were made at random and the hardness reported for the alloy is the average hardness.

The epsilon and sigma alloys were checked to see the extent of difference in hardness between the three phases. It was intended to use this method for differentiating between the alpha-plus-sigma and the alpha-plus-epsilon alloys in determining that portion of the diagram. However, the epsilon and sigma particles in the alloys concerned were so small that it was impossible to obtain reliable readings for them.

EXPERIMENTAL RESULTS

The results of the microscopic examinations and of the X-ray diffraction patterns are given in table 2. The isothermal section was drawn from these results. (See figs. 14 and 15). The table lists the alloys according to the phases they contain. The chemical composition found there is a corrected value. In all the analyses there was an insoluble material (chromium oxide, mainly) found in amounts varying from 0.18 to 2.76 percent; therefore, the chemical analyses were corrected so the alloying elements would add to 100 percent. The amounts of the phases expected from the phase diagram corresponding to the composition are given together with the amounts estimated from microscopic examination. The completed 1200° C isothermal section (fig. 14) shows that all alloys consisted of the phases known from the binary diagrams; no ternary phases were found. At 1200° C the alpha phase covers more than half of the area of the entire diagram. The existence of these extensive solid solutions is very significant from the practical point of view, as the chromium-cobalt-nickel alpha solid solutions form the matrix of several commercial heat-resisting alloys.

An interesting feature of the diagram is the deep penetration of the sigma phase into the ternary diagram. At 1200° C the sigma phase extends from the binary chromium-cobalt system to a ternary composition (point y, fig. 14) approximately corresponding to 21.5 percent nickel, 60.5 percent chromium, and 18 percent cobalt. The long and narrow field of the sigma phase extends roughly parallel to the cobalt-nickel side of the diagram. This expresses the fact that the chromium content increases only slightly, while about 55 percent of the cobalt content is replaced by nickel. The sigma-plus-alpha two-phase field extends more than two-thirds of the way to the chromium-nickel side of the diagram, so that alpha solid solutions with a nickel-cobalt ratio higher than 2 may coexist with the sigma phase. Since the solubility of the sigma phase in the alpha phase may be expected to decrease

considerably with decreasing temperature, the results indicate a strong possibility of precipitation of the brittle sigma phase even in alloys far removed from the chromium-cobalt binary system, such as those in the vicinity of point x in figure 14.

The alpha-sigma-epsilon three-phase field is quite narrow and its boundaries are as follows: The sigma corner (point y, fig. 14) 21.5 percent nickel, 18 percent cobalt, and 60.5 percent chromium; the epsilon corner (point z, fig. 14) 16.5 percent nickel, 12.5 percent cobalt, and 71 percent chromium, and the alpha corner (point x, fig. 14) 39 percent nickel, 16.5 percent cobalt, and 44.5 percent chromium. It is believed that the accuracy is within ±2 percent in composition since the final placement of the boundaries was accomplished by microscopic methods capable of detecting very small amounts of the phases.

The X-ray diffraction data given in figure 16 (data from table 6) lend further support to the location of the alpha corner of the three-phase field (x) at close to 16.5 percent cobalt. In this figure the a_o values for the saturated alpha solid solutions are shown to follow approximately two straight lines corresponding to the alpha-plus-sigma and the alpha-plus-epsilon boundaries. The intersection of these two straight lines at point x of the figure occurs at 17 percent cobalt which is in agreement with the value of 16.5 percent cobalt of the ternary diagram, within the experimental accuracy.

Tables 3 to 5 give typical X-ray diffraction patterns for the three phases with line number, distance from the knife edge in centimeters, values of θ, the radiation, indices h, k, and l for the epsilon and alpha patterns, and d values for the sigma lines. The variation of the d value for the twenty-seventh line of the sigma phase with varying composition is given in figure 17 from the data in table 7. Considerable variation in d values was found across the sigma field, with varying chromium content, when the nickel content was low. With increasing nickel content this variation decreases. The d value for the sigma phase saturated with alpha changes considerably with increasing nickel content. The two lines corresponding to the two boundaries of the sigma phase intersect at approximately 22 percent nickel, in agreement with the location of the end of the sigma phase (point y) in the phase diagram (fig. 14). In order to compare the chromium-cobalt-nickel sigma phase with the sigma phase of the chromium-iron system, filings from a 60-percent-chromium-plus-40-percent iron alloy were annealed at 650° C for $46\frac{1}{2}$ hours and then air-cooled.[1] A diffraction pattern was taken on these filings and upon comparing this pattern with the chromium-cobalt-nickel sigma pattern the ismorphism of the two lattices was confirmed, with a slight difference in lattice constants. The iron-chromium sigma phase gave a d value of 1.1827, as against a d value of 1.1816 for the chromium-cobalt-nickel sigma.

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[1]These filings were obtained from Mr. William J. Barnett of Case Institute of Technology.

In all the microstructures there were two impurity constituents seen in varying amounts. The dark dendrites shown in figure 18, embedded in a matrix of epsilon and sigma, are chromium-oxide particles. They usually have a characteristic "Chinese script" appearance and tend to concentrate at the top of the ingot. The slag particles shown in figure 19 are characterized by their round droplike shape. This photomicrograph taken at 500X shows an extremely large slag particle found in a homogenized specimen from alloy 67. Normally the slag particles are much smaller.

The typical microstructures of alpha-plus-sigma and sigma-plus-epsilon alloys often revealed cracks occurring through the sigma phase, as seen in figures 8 and 9. Both the alpha-plus-sigma alloys in figures 8 and 12 and the epsilon-plus-sigma alloys in figures 9 and 13 were etched electrolytically, followed with the alkaline permanganate stain. With this preparation the sigma phase always stained darker than the alpha and epsilon phases.

In all chromium-rich alloys a precipitate was seen in the epsilon matrix (figs. 6 and 7). In most alloys the precipitate particles had a characteristic platelike shape and well-developed orientation habits, as seen in the photomicrographs, suggesting that they were formed by either a martensite mechanism or Widmanstätten precipitation. The platelike precipitate is also seen in alloys of the epsilon-plus-sigma region. In figures 9 and 13 this is not clearly seen, as the particles are not resolved at 500X. In the epsilon-plus-alpha region a precipitate also occurs in the epsilon phase (fig. 10); however, the precipitate here forms extremely small particles, which cannot be resolved by the microscope even at high magnifications (fig. 20).

Several annealing treatments were tried to cause the platelike precipitate to coalesce, so that its identity could be more easily established. In alloy 18T36 (nominal composition 78 percent chromium, 11 percent cobalt, and 11 percent nickel) obtained from the General Electric Co., the precipitate in the epsilon phase was in the form of very large plates. The X-ray diffraction pattern, taken on powder from this specimen, gave an epsilon-plus-sigma pattern, although a thorough microscopic examination revealed no primary sigma particles. Accordingly, the sigma pattern must have originated with the platelike precipitated phase. The complete lack of coalescence of the sigma plates even in specimens given long time anneals (75 hr) at 1200° C suggests that the alloys may exist as solid solutions at that temperature and that the precipitate may form during quenching from the annealing temperature. The identity of the fine particles in the epsilon phase of the alpha-plus-epsilon alloys (fig. 10) is still unknown although it is probable that it consists of a precipitate of the alpha phase.

Since considerable difficulty was encountered with the microscopic examination of the alpha-plus-epsilon two-phase alloys, the X-ray diffraction work was expanded. Two different sets of powders for X-ray samples were taken from alloys 26, 40, 45, 56, 67, 71, and 74 and in all cases the X-ray diffraction pattern showed only the lines of the alpha and epsilon phases. This confirmed the previous investigation (reference 3) of the chromium-nickel binary diagram which also indicated only the two terminal phases in this system at 1200° C.

At some points in the work large discrepancies between the X-ray and microscopic methods were noted. In one case (alloy 54) microscopic examination gave 80 percent sigma and 20 percent alpha, while the X-ray diffraction pattern showed only alpha lines. An X-ray specimen was then prepared from unannealed powder. This gave a sharp sigma pattern and an alpha pattern with broad lines. It was found that the 1-hour annealing time at 1200° C for powders containing appreciable amounts of sigma phase was too long; the fine sigma powder had a tendency to sinter. By using shorter annealing time for the powders, or by using powders in the unannealed condition, the diffraction patterns were brought into agreement with the microscopic data.

With a few notable exceptions, there was close agreement between the amounts of phases determined in the microscopic work and the amounts of phases expected from the phase diagram. Differences were noted in alloys 70, 72, 46, and 42. Alloys 70 and 72 should be in the two-phase alpha-plus-sigma region according to the phase diagram and their chemical analyses. However, the microscopic examination and the X-ray diffraction pattern placed these two alloys in the two-phase alpha-plus-epsilon region. The alloys in question were homogenized for 75 hours and chemical-analysis rechecks were made, but the discrepancies were not eliminated. The two possible explanations are segregation or the effect of impurities in shifting the phase boundaries. Two spectrographic analyses were made on the samples and the amounts of impurities present were within the normal range found in all the alloys as shown in table 8. This makes the second alternative unlikely. There were appreciable differences between the original and the repeat chemical analyses of alloys 70 and 72. The second analysis for both gave about 5 percent less cobalt than the first one. This decrease in cobalt placed the alloys closer to the alpha-plus-epsilon two-phase region but the discrepancy still persisted.

In alloys 42 and 46, the anomalies were due to segregation in the ingot. After the 12-hour homogenizing period alloy 46 showed 80 percent epsilon and 20 percent sigma and alloy 42 showed 100 percent epsilon. After a 75-hour homogenizing cycle, the alloys still did not fall in line. Specimens taken from the bottom of these two ingots were, after the 75-hour homogenizing treatment, in good agreement with

the diagram; according to the microscopic examination alloy 46 was all epsilon and alloy 42 was 90 percent epsilon and 10 percent sigma.

The appearance of an unknown phase in some of the alloys (fig. 21) was another feature not explainable on the basis of the phase diagram. This phase, which was not attacked by any of the etching reagents used, formed idiomorphic dendrites, concentrated at the very bottom of some ingots. Samples taken from the bottom of several alloys spotted throughout the diagram were therefore examined. The unknown phase occurred in a very haphazard manner; it did not correlate with the ternary composition, although it appeared with greater frequency near the high-chromium corner of the diagram. The alloys of high chromium content melted at much higher temperatures than the other alloys and it was noted that the reaction with the crucible was much more pronounced in these alloys. From all these facts, it was concluded that the unknown phase was produced by an impurity, probably zirconium, reduced by the interaction of the melt with the crucible. To check this possibility further, a melt containing only electrolytic chromium was made under conditions similar to those normally encountered, except that it was overheated considerably. Examination of a specimen from this melt gave an eutecticlike structure of chromium and a non-etching second phase. A melt was then made using this contaminated chromium with additions of nickel and cobalt to produce an alloy in the epsilon-plus-sigma two-phase field. Upon examining the microstructure of this alloy, familiar idiomorphic dendrites of the unknown phase were present in large numbers.

The results of the work on microhardness testing are plotted in figure 22, from the data in table 9. This shows that the hardness of the saturated alpha phase is nearly constant until the cobalt content is approximately 40 percent. From 40 percent cobalt on to 58 percent cobalt the hardness of the alpha phase increases quite rapidly, as the saturated alpha phase of the chromium-cobalt binary system is approached. Two points, corresponding to alloys 51 (26.7 percent cobalt) and 75 (14.8 percent cobalt), gave alpha-phase hardness readings much higher than those expected from the curve. Microscopic examination of these alloys showed that the epsilon and sigma phases were finely distributed throughout the alpha matrix instead of being in large particles, as in the other alloys. The indentations made by the Tukon Hardness Tester encountered the small dispersed particles of the epsilon phase in alloy 75 and of the sigma phase in alloy 51.

DISCUSSION

From a practical point of view the most important part of the chromium-cobalt-nickel ternary system is the extensive alpha-solid-solution field. Several commercially important alloys for high-stress

service at high temperatures are based on the chromium-cobalt-nickel alpha phase, modified with additions of iron, tungsten, molybdenum, carbon, and so forth. A knowledge of the boundaries of this phase in the ternary system as well as in the presence of the above additions is, therefore, of considerable interest.

The deep penetration of the sigma phase into the ternary phase diagram is interesting in its theoretical aspects and also because of the practical difficulties it may cause. Massive or platelike particles of the brittle sigma phase should be excluded from all commercial alloys. The ternary diagram shows that alloys with an alpha matrix may contain some of this compound even in a composition range far removed from the chromium-cobalt binary alloys, for instance, with a nickel-cobalt ratio higher than 2. The fact that the sigma lattice is sustained even when well over half of the cobalt atoms in it are replaced by nickel atoms clearly indicates that nickel itself has a certain tendency to form the sigma phase with chromium. This tendency is hidden in the binary chromium-nickel alloys, where the sigma phase is not known to occur, but it becomes operative in the presence of a sufficient amount of cobalt. The interpretation of these facts in terms of electron concentrations is rendered difficult by the uncertainty of the present knowledge of the valency electron structure of the transition elements in their alloys.

Most alloys consisting of the epsilon phase were found to be quite brittle. Examination of their fractured surface showed a cleavage pattern which, by all appearances, corresponded to the platelike sigma precipitate found in these alloys. It is, therefore, very probable that the brittleness of the chromium-rich ternary alloys resulted from the precipitated brittle sigma-phase particles. Chromium metal itself, when melted and annealed according to the procedure used for the alloys, did not contain platelike precipitate and did not become brittle. In view of these observations and of the identification of this precipitate phase by X-ray diffraction, the interpretation by Elsea, Westerman, and Manning (reference 1) as chromium nitride of what appears to be the same platelike precipitate in binary chromium-cobalt alloys is probably incorrect. It is posible that nitrogen does play a role to the extent of affecting the precipitation of the sigma phase, as it does in iron-chromium alloys (reference 5).

Recent work at Notre Dame, not included in this report, suggests a decrease in solubility of sigma in the alpha phase with decreasing temperature. In order to check the possibility of an embrittling sigma precipitation in the alpha phase, similar to that just described for the epsilon phase, specimens from the alloys near the alpha boundary of the alpha-plus-sigma two-phase field were given a special heat treatment. This treatment consisted of homogenizing the alloys at 1200° C for 12 hours, then lowering the temperature at 100° C

intervals every $1\frac{1}{2}$ hours until 800° C was reached. From that temperature the samples were water-quenched. They were then examined to detect the presence of any precipitate in the alpha matrix. The only change noted was an increase in the amount of the sigma phase, but no sigma precipitate was observed in the alpha matrix.

In the high-cobalt binary cobalt-chromium alloys the beta phase could be identified by X-ray diffraction after homogenizing at 1200° C and quenching. In accordance with Troiano and Tokich (reference 6), this may be interpreted as a result of a martensite transformation during quenching. However, alloys with 10 percent nickel or more did not show the beta phase upon quenching to room temperature. According to a personal communication from Mr. A. R. Elsea, similar results were obtained in unpublished work at Battelle Memorial Institute.

The results of the present work are in fairly good agreement with previous investigations of the three binary systems concerned. In accordance with Jenkins, Bucknall, Austin, and Mellor (reference 3) the chromium-nickel binary system was found to have at 1200° C no other phases between the alpha and epsilon terminal solid solutions. The solubility limit for the epsilon phase appears to be near 19 percent nickel and that for the alpha phase, near 58 percent nickel. The agreement with the work of Elsea, Westerman, and Manning (reference 1) on the cobalt-chromium binary diagram is very good throughout, with the exception of the solubility limit of the chromium-rich solid solutions. For 1200° C this limit is given by the above-named authors at 31 percent cobalt, whereas the present work clearly indicates that it should be placed at 25 percent cobalt.

The series of alloys obtained from the General Electric Co. were treated and studied in the same way as those melted in this laboratory. The results were in good agreement with the phase diagram given in figures 14 and 15. However, discrepancies were found in the relative amounts of the phases, estimated microscopically, as compared with the amounts expected from the ternary diagram. These discrepancies could be accounted for, since the General Electric alloys were placed in the ternary diagram according to their nominal compositions, no actual chemical analyses being available for most of them.

CONCLUSIONS

A survey of the chromium-cobalt-nickel ternary phase diagram at 1200° C has been made by means of microscopic and X-ray diffraction studies on 110 vacuum-melted alloys prepared from commercial metals

of the highest purity available. At 1200° C the following phases occur: (1) Very extensive face-centered cubic solid solutions, based on the binary cobalt-nickel solid solutions, (2) body-centered cubic chromium-base solid solutions, and (3) brittle sigma solid solutions, based on the chromium-cobalt sigma phase which is isomorphous with the iron-chromium sigma phase. In the sigma solid solutions well over half of the cobalt can be replaced by nickel with relatively little change in the chromium content. The diagram indicates that the sigma phase may coexist with alpha of a nickel-cobalt ratio higher than 2. The brittleness of alloys consisting essentially of the epsilon phase is correlated with the platelike precipitate of sigma in these alloys which is not suppressed by quenching.

University of Notre Dame
Notre Dame, Ind., January 31, 1949

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TABLE 1

ANALYSIS OF MATERIALS USED

Element or compound	Electrolytic chromium	Electrolytic nickel	Cobalt rondelles
C	0.01	----------	0.17
S	.012	0.001	.009
Fe	.06	.01	.12
Cu	Trace	.01	.02
Pb	.001	----------	-----
O_2	.51	----------	-----
H_2	.045	----------	-----
N_2	.010	----------	-----
CaO	-----	----------	.12
MgO	-----	----------	.04
Mn	-----	----------	.06
SiO_2	-----	----------	.13
Cr	Bal.	----------	-----
Co	-----	0.6 to 0.8	Bal.
Ni	-----	Bal.	.46

TABLE 2

RESULTS OF MICROSCOPIC EXAMINATIONS AND X-RAY

DIFFRACTION STUDIES

Alloy	Chemical composition (percent) (a)			Phases from diagram (percent)			Phases found – Microscopic examination (percent)			Phases found – X-ray	Remarks
	Ni	Co	Cr	Epsilon	Alpha	Sigma	Epsilon	Alpha	Sigma		
Alpha alloys											
1	35.6	35.8	28.6	——	100	——	——	100	——	Alpha	No C added, no sleeve, zirconia crucible
9	(b)	(b)	(b)	——	100	——	——	100	——	Alpha	No C added, no sleeve, magnesia crucible
10	(b)	(b)	(b)	——	100	——	——	100	——	Alpha	Do.
11	(b)	(b)	(b)	——	100	——	——	100	——	Alpha	C added to Co, no sleeve, magnesia crucible
12	(b)	(b)	(b)	——	100	——	——	100	——	Alpha	Do.
15	(b)	(b)	(b)	——	100	——	——	100	——	Alpha	C added to Cr, no sleeve, magnesia crucible
Alpha-plus-sigma alloys											
2	17.2	44.2	38.6	——	100	——	——	100	——	Alpha	No C added, no sleeve, zirconia crucible
[c]2	17.2	44.2	38.6	——	100	——	——	100	Trace	Alpha	Do.
3	11.7	45.5	42.8	——	80	20	——	80	20	[d]Alpha	Do.
4	14.9	37.2	47.9	——	50	50	——	40	60	Alpha, sigma	Do.
5	15.1	27.7	57.2	——	2	98	——	20	80	Alpha, sigma	Do.
[c]5	15.1	27.7	57.2	——	2	98	——	Trace	100	Alpha, sigma	Do.
14	——	50.0	50.0	——	20	80	——	15	85	Alpha, sigma	C added to Co, no sleeve, zirconia crucible
22	4.5	45.4	50.1	——	20	80	——	30	70	Alpha, sigma	C added to Cr no sleeve, zirconia crucible
28	——	57.9	42.1	——	70	30	——	65	35	Alpha, sigma	C added to Cr, graphite sleeve, zirconia crucible
29	3.9	54.0	42.1	——	70	30	——	80	20	Alpha, sigma	Do.
30	(b)	(b)	(b)	——	40	60	——	50	50	Alpha, sigma	Do.
31	3.5	53.4	43.1	——	60	40	——	70	30	Alpha, sigma	Do.
32	4.7	46.4	48.9	——	40	60	——	30	70	Alpha, sigma	C added to Cr, No sleeve, zirconia crucible
33	6.2	43.3	50.5	——	30	70	——	40	60	Alpha, sigma	Do.
35	6.5	42.3	51.2	——	20	80	——	40	60	Alpha, sigma	Do.
41	22.0	15.6	62.4	(e)	(e)	(e)	——	30	70	Alpha, sigma	No C added, graphite sleeve and cover, zirconia crucible
[c]41	22.0	15.6	62.4	(e)	(e)	(e)	——	30	70	Alpha, sigma	Do.
47	27.4	20.9	51.7	——	50	50	——	60	40	Alpha, sigma	Do.
48	22.9	28.9	48.2	——	60	40	——	70	30	[d]Alpha	Do.
49	10.5	50.8	38.7	——	95	5	——	100	Trace	[d]Alpha	Do.
[c]49	10.5	50.8	38.7	——	95	5	——	90	10	Alpha	Do.
50	36.0	18.6	45.4	——	90	10	——	95	5	Alpha	Do.
[c]50	36.0	18.6	45.4	——	90	10	——	90	10	Alpha	Do.
51	30.8	26.7	42.5	——	90	10	——	95	5	Alpha	Do.
[c]51	30.8	26.7	42.5	——	90	10	——	95	5	Alpha	Do.
54	28.8	16.2	55.0	——	10	90	——	20	80	[d]Alpha, sigma	Do.
57	22.0	19.0	59.0	——	5	95	——	10	90	Alpha, sigma	Do.
58	15.1	27.4	57.5	——	2	98	——	2	98	Sigma	Do.
59	22.4	26.9	50.7	——	40	60	——	40	60	Alpha	Do.
60	20.2	32.5	47.3	——	60	40	——	50	50	Alpha, sigma	Do.
61	30.0	24.5	45.5	——	80	20	——	90	10	Alpha	Do.
62	15.0	34.1	50.9	——	30	70	——	20	80	Alpha, sigma	Do.
63	10.4	38.4	51.2	——	30	70	——	20	80	Alpha, sigma	Do.
68	27.8	17.8	54.4	——	50	50	——	80	20	Alpha	Do.
69	22.3	21.9	55.8	——	20	80	——	30	70	Sigma	Do.
86	27.0	32.3	40.7	——	100	Trace	——	100	Trace	Alpha	Do.
[c]86	27.0	32.3	40.7	——	100	Trace	——	90	10	—do—	Do.
87	19.8	40.9	39.3	——	100	Trace	——	100	Trace	—do—	Do.
[c]87	19.8	40.9	39.3	——	100	Trace	——	95	5	—do—	Do.
88	4.1	58.3	37.6	——	100	Trace	——	100	Trace	—do—	Do.
[c]88	4.1	58.3	37.6	——	100	Trace	——	98	2	—do—	Do.
104	——	65.1	34.9	——	100	Trace	——	100	Trace	—do—	Do.
106	36.7	17.6	45.7	——	90	10	——	90	10	—do—	Do.

[a]Chemical composition given is corrected composition.

[b]No analysis.

[c]75-hr-homogenized specimen; others were 12-hr-homogenized specimens.

[d]Diffraction patterns from annealed powders gave only alpha lines; diffraction patterns made with unannealed powders showed also sigma lines, in agreement with microscopic results (see section "X-Ray Analysis").

[e]Three-phase alloy.

TABLE 2 - Continued

RESULTS OF MICROSCOPIC EXAMINATIONS AND X-RAY

DIFFRACTION STUDIES - Continued

Alloy	Chemical composition (percent) (a)			Phases from diagram (percent)			Phases found - Microscopic examination (percent)			X-ray	Remarks
	Ni	Co	Cr	Epsilon	Alpha	Sigma	Epsilon	Alpha	Sigma		
Alpha-plus-epsilon alloys											
17	46.8	8.3	44.9	—	100	—	Trace	100	—	Alpha	C added to Cr, no sleeve, magnesia crucible
18	39.2	8.1	52.7	20	80	—	20	80	—	Alpha	C added to Cr, no sleeve, zirconia crucible
26	25.7	1.0	73.3	80	20	—	70	30	—	Alpha, epsilon	C added to Cr, graphite sleeve, zirconia crucible
[c]26	25.7	1.0	73.3	80	20	—	70	30	—	Alpha, epsilon	Do.
27	49.2	.3	50.5	15	85	—	15	85	—	Alpha	Do.
40	27.1	9.3	63.6	70	30	—	90	10	—	Alpha, epsilon	No C added, graphite sleeve and cover, zirconia crucible
45	19.1	6.4	74.5	95	5	—	95	5	—	Alpha, epsilon	Do.
[c]45	19.1	6.4	74.5	95	5	—	98	2	—	Alpha, epsilon	Do.
56	.8	57.7	57.7	40	60	—	50	50	—	Alpha, epsilon	Do.
[c]56	.8	57.7	57.7	40	60	—	40	60	—	Alpha, epsilon	Do.
67	26.0	12.6	61.4	60	40	—	60	40	—	Alpha, epsilon	Do.
[c]67	26.0	12.6	61.4	60	40	—	60	40	—	Alpha, epsilon	Do.
70	20.9	23.5	55.6	—	80	20	35	65	—	Alpha, epsilon	Do.
[c]70	20.9	23.5	55.6	—	80	20	35	65	—	Alpha, epsilon	Do.
70	24.5	19.8	55.7	—	80	20	35	65	—	Alpha, epsilon	Do.
[c]70	24.5	19.8	55.7	—	80	20	40	60	—	Alpha, epsilon	Do.
71	27.3	12.1	60.6	60	40	—	50	50	—	Alpha, epsilon	Do.
[c]71	27.3	12.1	60.6	60	40	—	70	30	—	Alpha, epsilon	Do.
72	19.7	25.0	55.3	—	80	20	30	70	—	Alpha, epsilon	Do.
[c]72	19.7	25.0	55.3	—	80	20	30	70	—	Alpha, epsilon	Do.
72	24.2	20.4	55.4	—	80	20	30	70	—	Alpha, epsilon	Do.
[c]72	24.2	20.4	55.4	—	80	20	30	70	—	Alpha, epsilon	Do.
73	18.4	----	81.6	100	Trace	—	100	Trace	—	Epsilon	Do.
74	36.8	5.1	58.1	60	40	—	60	40	—	Alpha, epsilon	Do.
75	38.8	14.8	46.4	10	90	—	10	90	—	Alpha	Do.
[c]75	38.8	14.8	46.4	10	90	—	10	90	—	Alpha	Do.
78	18.0	9.7	72.3	95	5	—	100	Trace	—	Alpha, epsilon	Do.
79	17.7	9.3	73.0	98	2	—	95	5	—	Alpha, epsilon	Do.
84	35.5	15.1	49.5	20	80	—	10	90	—	Alpha	Do.
85	39.0	10.8	50.2	15	85	—	20	80	—	Alpha	Do.
89	54.0	.3	45.7	5	95	—	Trace	100	—	Alpha	Do.
[c]89	54.0	.3	45.7	5	95	—	10	90	—	Alpha	Do.
90	50.2	4.8	45.0	Trace	100	—	Trace	100	—	Alpha	Do.
[c]90	50.2	4.8	45.0	Trace	100	—	5	95	—	Alpha	Do.
102	20.9	.2	78.9	95	5	—	100	Trace	—	Epsilon	Do.
Epsilon-plus-sigma alloys											
7	13.7	17.6	68.7	70	—	30	80	—	20	Epsilon, sigma	No C added, no sleeve, zirconia crucible
16	—	25.8	74.2	95	—	5	90	—	10	Epsilon, sigma	C added to Cr, no sleeve, zirconia crucible
[c]16	—	25.8	74.2	95	—	5	90	—	10	Epsilon, sigma	Do.
20	4.2	31.3	64.5	30	—	70	20	—	80	Epsilon, sigma	Do.
25	9.1	23.6	67.3	60	—	40	50	—	50	Epsilon, sigma	C added to Cr, graphite sleeve, zirconia crucible
34	7.5	30.9	61.6	10	—	90	10	—	90	Sigma	C added to Cr, No sleeve, zirconia crucible
36	—	33.8	66.2	50	—	50	60	—	40	Epsilon, sigma	Do.
38	18.1	20.4	61.8	Trace	—	100	5	—	95	Epsilon, sigma	No C added, graphite sleeve and cover, zirconia crucible
43	12.8	23.8	63.4	20	—	80	20	—	80	Epsilon, sigma	Do.

[a]Chemical composition given is corrected composition.

[c]75-hr-homogenized specimen; others were 12-hr-homogenized specimens.

TABLE 2.- Concluded

RESULTS OF MICROSCOPIC EXAMINATIONS AND X-RAY

DIFFRACTION STUDIES - Concluded

Alloy	Chemical composition [1] (percent) (a)			Phases from diagram (percent)			Phases found - Microscopic examination (percent)			X-ray	Remarks
	Ni	Co	Cr	Epsilon	Alpha	Sigma	Epsilon	Alpha	Sigma		
Epsilon-plus-sigma alloys											
44	15.8	22.6	61.6	5	—	95	10	—	90	Sigma	No C added, graphite sleeve and cover, zirconia crucible
46	10.0	10.0	80.0	100	—	—	80	—	20	Epsilon, sigma	Do.
[c]46	10.0	10.0	80.0	100	—	—	80	—	20	Epsilon, sigma	Do.
52	9.2	19.1	71.7	90	—	10	80	—	20	Epsilon, sigma	Do.
55	19.8	13.2	67.0	—	—	—	60	—	40	Epsilon, sigma	Do.
64	15.4	22.1	62.5	15	—	85	10	—	90	Sigma	Do.
65	8.4	27.8	63.8	10	—	90	5	—	95	Sigma	Do.
66	20.7	18.0	61.3	20	—	80	15	—	85	Epsilon, sigma	Do.
77	14.5	20.5	65.0	40	—	60	50	—	50	Epsilon, sigma	Do.
82	19.0	17.7	63.3	30	—	70	40	—	60	Sigma	Do.
83	20.6	17.5	61.9	Trace	—	100	Trace	—	100	Sigma	Do.
[c]83	20.6	17.5	61.9	Trace	—	100	Trace	—	100	Sigma	Do.
103	—	27.9	72.1	75	—	25	60	—	40	Epsilon, sigma	Do.
[c]103	—	27.9	72.1	75	—	25	70	—	30	Epsilon, sigma	Do.
105	15.3	13.5	71.2	95	—	5	90	—	10	Epsilon, sigma	Do.
[c]105	15.3	13.5	71.2	95	—	5	90	—	10	Epsilon, sigma	Do.
113	6.1	24.9	69.0	80	—	20	100	—	Trace	Epsilon	Do.
116	—	27.3	72.7	90	—	10	100	—	Trace	Epsilon	Do.
[c]116	—	27.3	72.7	90	—	10	95	—	5	Epsilon	Do.
Epsilon alloys											
19	6.1	17.9	76.0	100	—	—	100	—	—	Epsilon	C added to Cr, no sleeve, zirconia crucible
[c]19	6.1	17.9	76.0	100	—	—	100	—	Trace	Epsilon	Do.
37	15.0	12.4	72.6	100	—	—	100	—	—	Epsilon	No C added, graphite sleeve and cover, zirconia crucible
[c]37	15.0	12.4	72.6	100	—	—	100	—	—	Epsilon	Do.
39	15.4	6.4	78.2	100	—	—	100	—	—	Epsilon	Do.
[c]39	15.4	6.4	78.2	100	—	—	100	Trace	—	Epsilon	Do.
42	5.1	24.9	70.0	70	—	30	100	—	—	Epsilon	Do.
[c]42	5.1	24.9	70.0	70	—	30	100	—	—	Epsilon	Do.
76	11.1	20.9	68.0	60	—	40	100	—	—	Epsilon	Do.
80	16.6	11.7	71.7	100	—	—	100	—	—	Epsilon	Do.
81	19.0	9.6	71.4	95	5	—	100	—	—	Epsilon	Do.
[c]81	19.0	9.6	71.4	95	5	—	100	Trace	—	Epsilon	Do.
Sigma alloys											
21	4.4	38.6	57.0	—	—	100	—	5	95	Sigma	C added to Cr, no sleeve, zirconia crucible
[c]21	4.4	38.6	57.0	—	—	100	—	—	100	Sigma	Do.
24	8.3	33.7	58.0	—	—	100	—	—	100	Sigma	No C added, graphite sleeve and cover, zirconia crucible
[c]24	8.3	33.7	58.0	—	—	100	—	—	100	Sigma	Do.
112	—	43.3	56.7	—	—	100	—	—	100	Sigma	Do.
[c]112	—	43.3	56.7	—	—	100	—	—	100	Sigma	Do.

[a]Chemical composition given is corrected composition.

[c]75-hr-homogenized specimen; others were 12-hr-homogenized specimens.

TABLE 3

TYPICAL ALPHA PATTERN FROM ALLOY 2 WITH

FACE-CENTERED CUBIC CRYSTAL STRUCTURE

Line	Intensity	Distance (cm)	θ	$\sin^2\theta$	hkl	Radiation
1	Medium	21.18	30°19'	0.2548	111	Beta
2	Dark	23.51	33°41'	.3076	111	Alpha
3	Light	24.91	35°41'	.3402	200	Beta
4	Medium	27.81	39°49'	.4100	200	Alpha
5	Light	38.73	55°28'	.6787	220	Beta
6	Dark	45.24	64°48'	.8187	220	Alpha
7	Dark	45.36	64°58'	.8210	220	$Alpha_2$
8	Light	52.66	75°24'	.9365	311	Beta

TABLE 4

TYPICAL EPSILON PATTERN FROM ALLOY 19 WITH

BODY-CENTERED CUBIC CRYSTAL STRUCTURE

Line	Intensity	Distance (cm)	θ	$\sin^2\theta$	hkl	Radiation
1	Medium	21.49	30°46'	0.2617	110	Beta
2	Dark	23.89	34°13'	.3162	110	Alpha
3	Light	32.45	47°4'	.5360	200	Beta
4	Medium	36.80	52°44'	.6334	200	Alpha
5	Medium	36.88	52°50'	.6518	200	$Alpha_2$
6	Light	43.59	62°27'	.7861	211	Beta
7	Dark	54.08	77°28'	.9531	211	Alpha
8	Dark	54.24	77°41'	.9615	211	$Alpha_2$

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TABLE 5

TYPICAL SIGMA PATTERN FROM ALLOY 24 OF

UNKNOWN CRYSTAL STRUCTURE

Line	Intensity	Distance (cm)	θ	$\sin^2\theta$	d value	Radiation
1	Light	20.30	29°3'	0.4856	2.1423	Beta
2	Medium	21.04	30°8'	.5020	2.2734	Alpha
3	Light	21.56	30°53'	.5133	2.0267	Beta
4	Light	22.26	31°52'	.5279	1.9706	Beta
5	Dark	22.76	32°36'	.5388	2.1181	Alpha
6	Medium	23.39	33°31'	.5522	2.0668	Alpha
7	Dark	24.06	34°27'	.5657	2.0174	Alpha
8	Dark	24.77	35°29'	.5805	1.9660	Alpha
9	Dark	25.36	36°20'	.5925	1.9262	Alpha
10	Medium	26.07	37°19'	.6062	1.8826	Alpha
11	Light	26.90	38°31'	.6227	1.8328	Alpha
12	Light	28.31	40°34'	.6503	1 7550	Alpha
13	Dark	41.68	59°42'	.8634	1.3218	Alpha
14	Medium	45.86	65°40'	.9112	1.2525	Alpha
15	Medium	45.99	65°50'	.9124	1.2541	Alpha
16	Light	47.41	67°53'	.9264	1.2319	Alpha
17	Light	47.58	68°8	.9281	1.2328	Alpha
18	Medium	47.75	68°25'	.9289	1.2273	Alpha
19	Medium	47.96	68°42'	.9317	1.2281	Alpha
20	Light	48.44	69°23'	.9359	1.1116	Beta
21	Light	48.75	69°50'	.9387	1.2158	Alpha
22	Light	48.95	70°8'	.9405	1.2166	Alpha
23	Light	49.95	71°	.9455	1.2070	Alpha
24	Light	50.12	71°47'	.9499	1.2046	Alpha
25	Light	50.85	72°49'	.9554	1.1945	Alpha
26	Light	51.10	73°10'	.9571	1.1955	Alpha
27	Light	52.38	75°	.9659	1.1816	Alpha
28	Light	52.64	75°24'	.9677	1.1824	Alpha
29	Light	53.85	77°7'	.9748	1.1707	Alpha
30	Light	54.13	77°31'	.9764	1.1718	Alpha

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TABLE 6

VALUES OF a_o FOR ALPHA BOUNDARY ALLOYS

Alloy	Chemical composition (percent)			Phases in alloy	a_o
	Ni	Co	Cr		
89	54.0	0.3	45.7	Alpha plus epsilon	3.5718
90	50.2	4.8	45.0	Alpha plus epsilon	3.5718
75	38.8	14.8	46.4	Alpha plus epsilon	3.5766
106	36.7	17.6	45.7	Alpha plus sigma	3.5767
50	36.0	18.6	45.4	Alpha plus sigma	3.5779
51	30.8	26.7	42.5	Alpha plus sigma	3.5765
86	27.0	32.3	40.7	Alpha plus sigma	3.5705
87	19.8	40.9	39.3	Alpha plus sigma	3.5697
2	17.2	44.2	38.6	Alpha plus sigma	3.5665
49	10.5	50.8	38.7	Alpha plus sigma	3.5665
88	4.1	58.3	37.6	Alpha plus sigma	3.5594

TABLE 7

SIGMA ALLOYS USED FOR DETERMINING d VALUES

Alloy	Chemical composition (percent)			Phases in alloy	d values[1] for twenty-seventh line
	Ni	Cr	Co		
36	----	33.8	66.2	Epsilon plus sigma	1.1822
20	4.2	31.3	64.5	Epsilon plus sigma	1.1822
44	15.8	22.6	61.6	Epsilon plus sigma	1.1819
82	19.0	17.7	63.3	Epsilon plus sigma	1.1823
83	20.6	17.5	61.9	Sigma plus trace of epsilon	1.1816
66	20.7	18	61.3	Epsilon plus sigma	1.1816
14	0	50	50	Alpha plus sigma	1.1785
33	6.2	43.3	50.5	Alpha plus sigma	1.1796
5	15.1	27.7	57.2	Alpha plus sigma	1.1806
57	22.0	19.0	59.0	Alpha plus sigma	1.1816
24	8.3	33.7	58	Sigma	1.1816

[1]Calculated using twenty-seventh line of sigma pattern. For comparison, sigma pattern of alloy containing 60 percent chromium and 40 percent iron gave d value of 1.1827.

TABLE 8

NORMAL RANGE OF SEMIQUANTITATIVE

SPECTROGRAPHIC ANALYSES

Element[a]	Concentration[b]
Chromium	Major
Cobalt	Major
Nickel	Major
Iron	0.00X to 0.0X
Silicon	Not found to 0.0X
Copper	0.00X to 0.0X
Manganese	0.00X to 0.0X
Lead	0.00X
Aluminum	Not found to 0.00X[c]
Magnesium	Not found to 0.00X[c]
Titanium	Not found to 0.00X
Zirconium	Not found to 0.X

[a]Elements checked but not found: Molybdenum, vanadium, tin, zinc, and bismuth.

[b]0.X, 0.0X, and 0.00X give concentration of elements estimated to the nearest decimal place.

[c]When magnesia crucibles were used, aluminum and magnesium ran on high side of 0.X.

TABLE 9

KNOOP HARDNESS OF ALPHA PHASE

OF ALPHA BOUNDARY ALLOYS

Alloy	Chemical composition (percent)			Knoop hardness number
	Ni	Co	Cr	
2	17.2	44.2	38.6	290
49	10.5	50.8	38.7	324
50	36.0	18.6	45.4	268
51	30.8	26.7	42.5	326
75	38.8	14.8	46.4	342
86	27.0	32.3	40.7	242
87	19.8	40.9	39.3	269
88	4.1	58.3	37.6	470
89	54.0	.3	45.7	252
90	50.2	4.8	45.0	253

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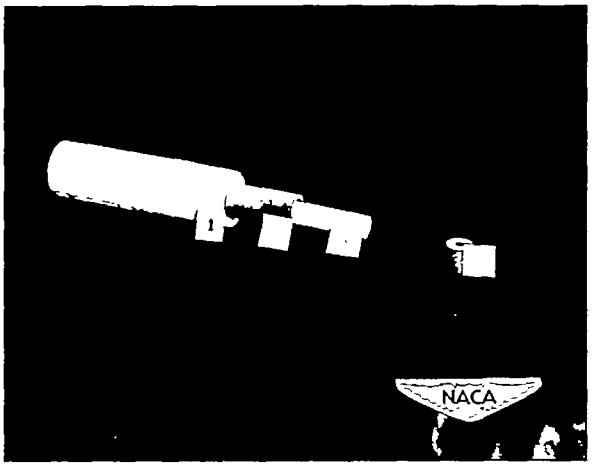

Figure 1.- Sleeve arrangement with (1) silica sleeve, (2) graphite crucible, (3) zirconia crucible, and (4) graphite cover.

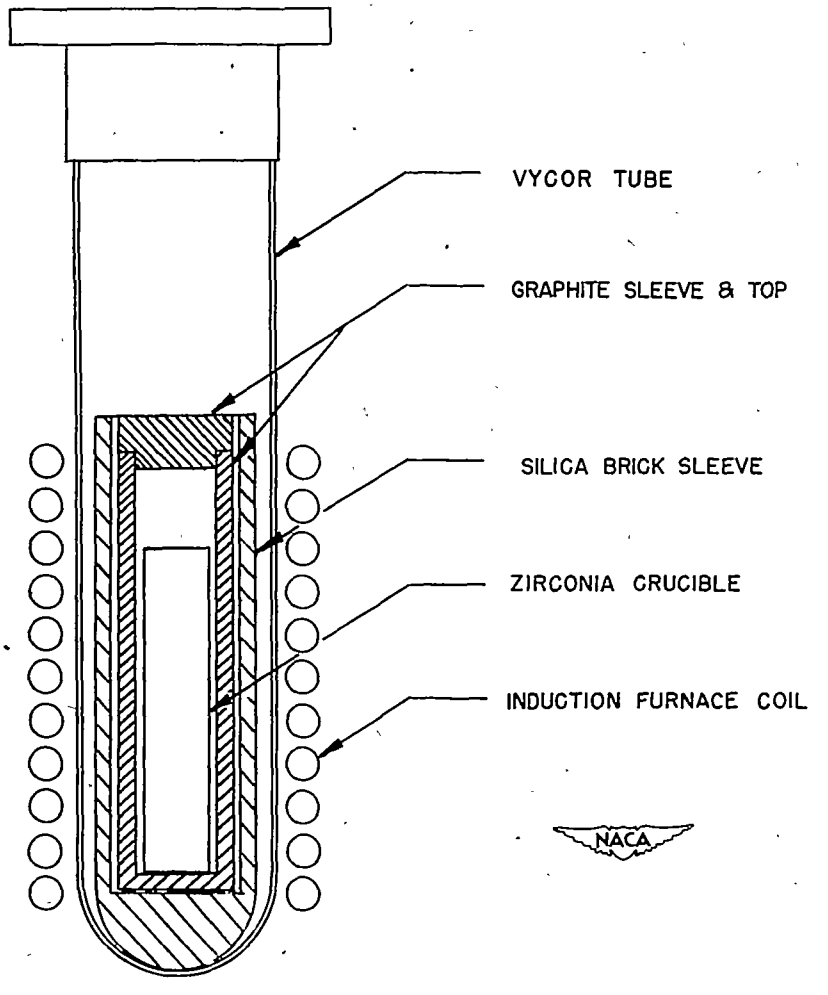

Figure 2.- Longitudinal cross section of Vycor tube of induction furnace.

Figure 3.- Vacuum induction furnace.

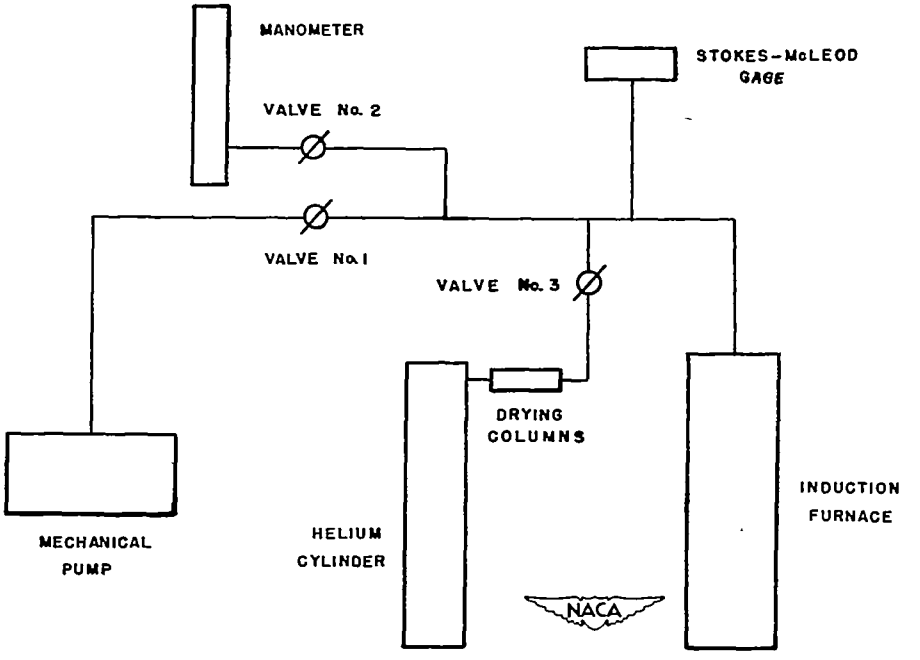

Figure 4.- Schematic diagram of vacuum induction furnace.

Figure 5.- Homogenizing furnaces.

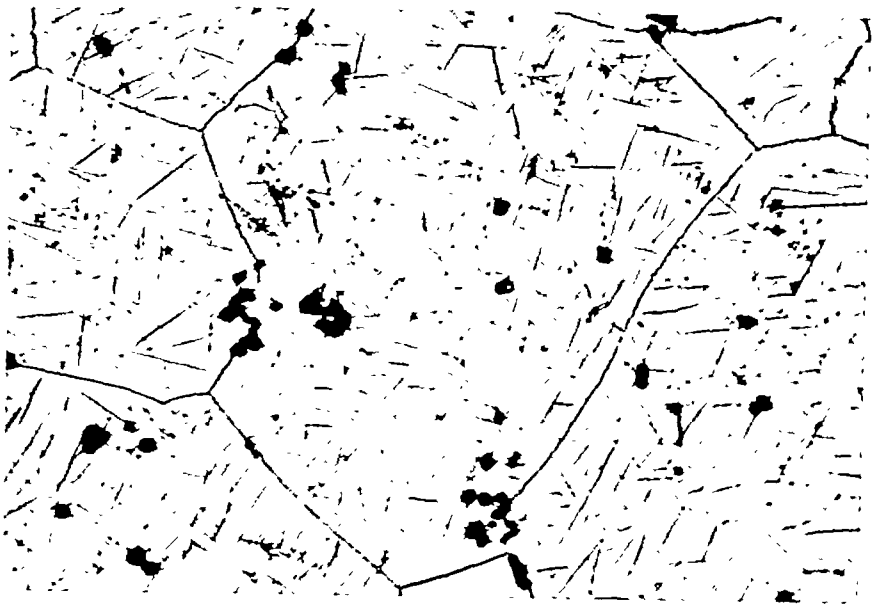

Figure 6.- Alloy 18T36 with nominal composition of 11 percent nickel, 11 percent cobalt, and 78 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1 without alkaline permanganate stain; X500. Epsilon phase with platelike sigma precipitate; also scattered chromium-oxide inclusions.

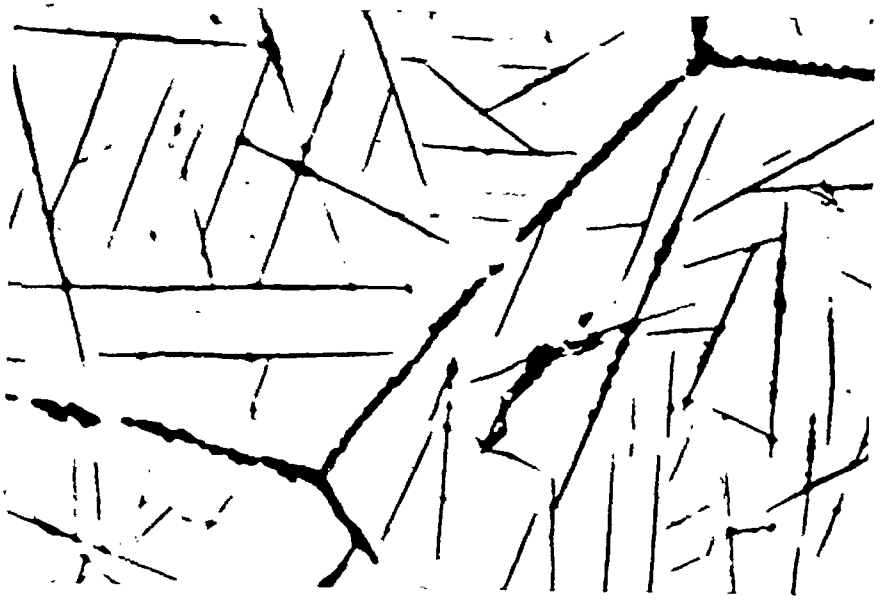

Figure 7.- Alloy 18T36 with nominal composition of 11 percent nickel, 11 percent cobalt, and 78 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1 without alkaline permanganate stain; X2500. Note that sigma-precipitate needles do not extend to grain boundaries.

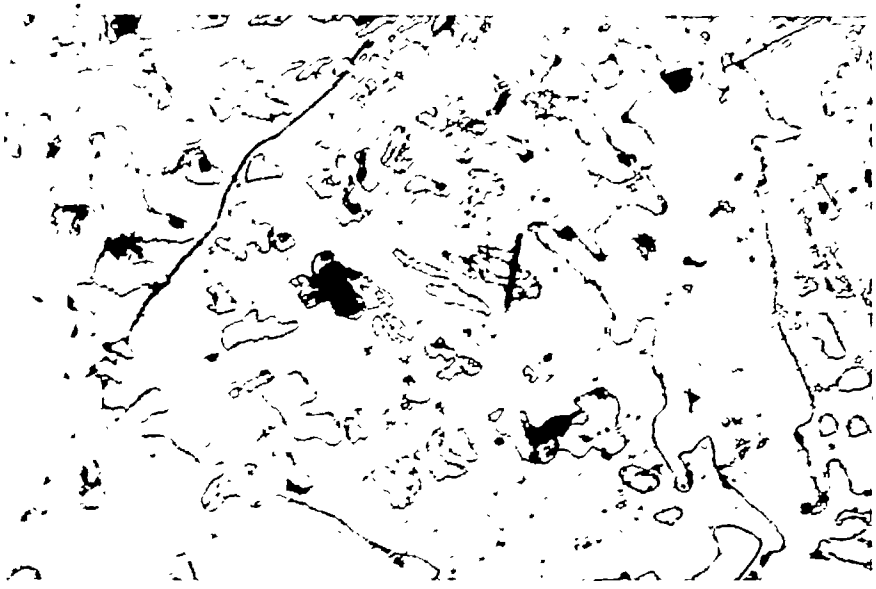

Figure 8.- Alloy 62 containing 15 percent nickel, 34.1 percent cobalt, and 50.9 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1; X500. Note crack in dark-stained sigma.

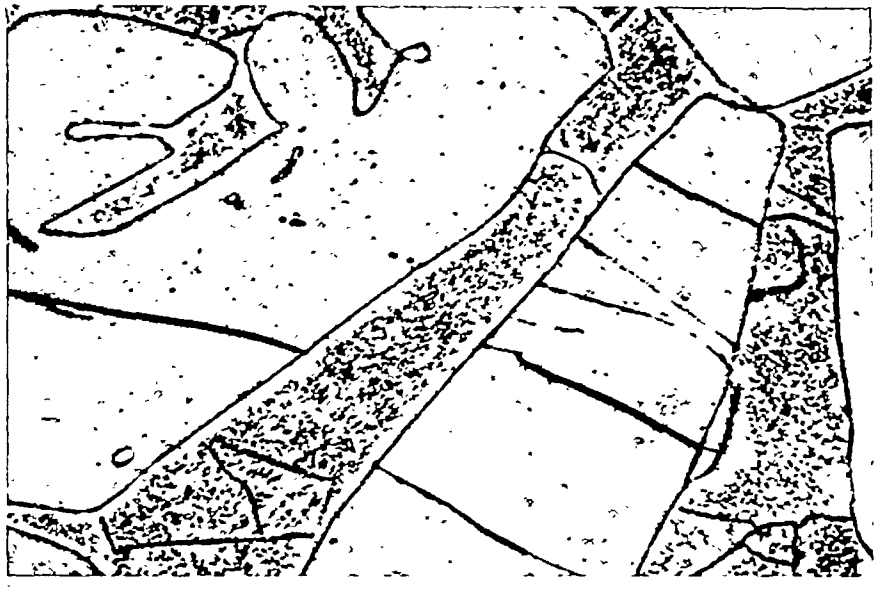

Figure 9.- Alloy 43 containing 12.8 percent nickel, 23.8 percent cobalt, and 63.4 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1; X500. Sigma stained dark, epsilon with incompletely resolved sigma precipitate. Note large number of cracks in sigma phase and cracks in epsilon also.

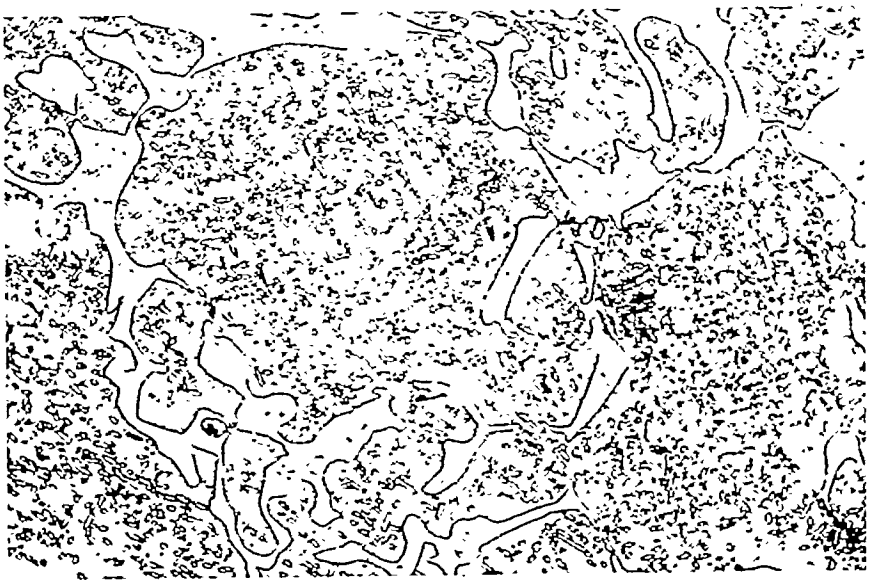

Figure 10.- Alloy 74 containing 36.8 percent nickel, 5.1 percent cobalt, and 58.1 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1 without alkaline permanganate stain; X500. Dark-stained alpha with fine epsilon precipitate; light primary epsilon phase with very fine, incompletely resolved alpha precipitate.

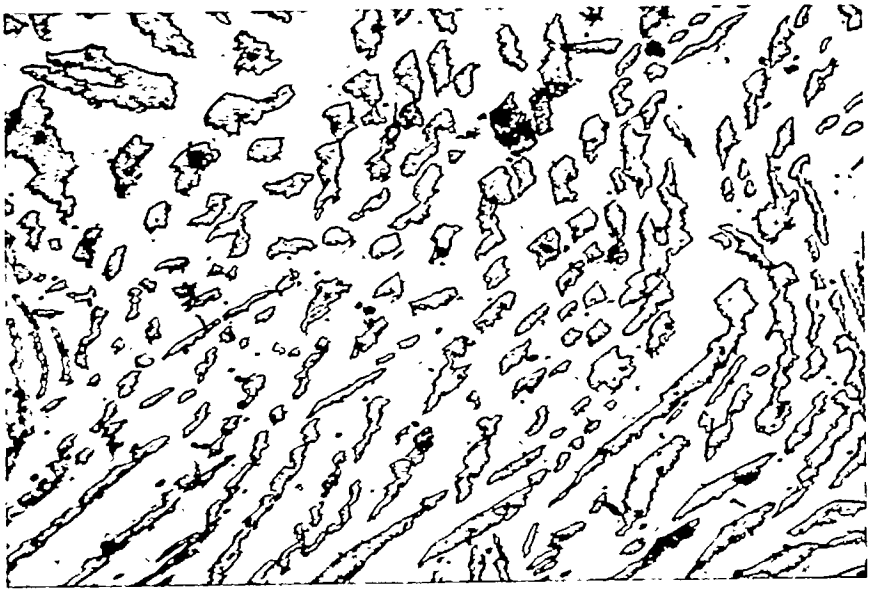

Figure 11.- Alloy 71 containing 27.3 percent nickel, 12.1 percent cobalt, and 60.6 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 3; X500. Epsilon stained dark; alpha did not stain.

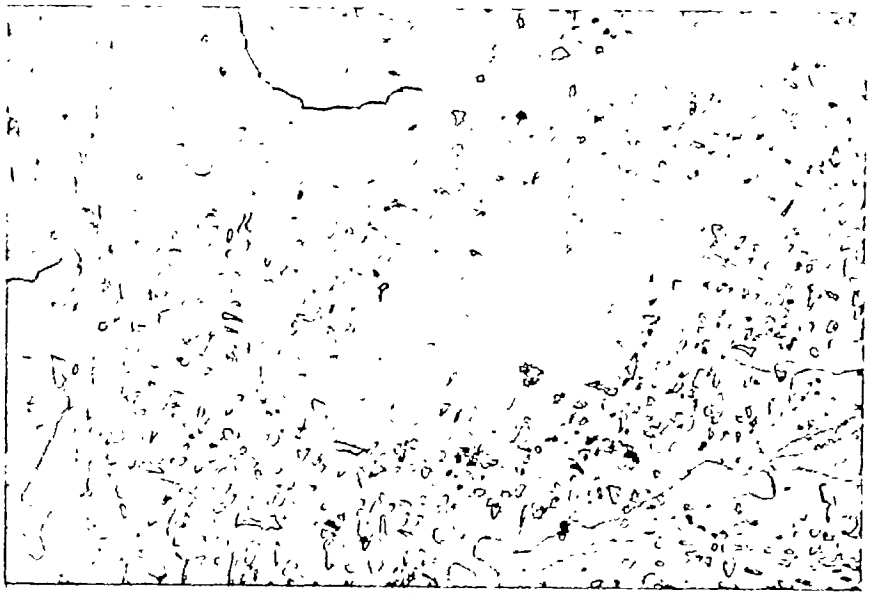

Figure 12.- Alloy 50 containing 36 percent nickel, 18.6 percent cobalt, and 45.4 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1; X500. Sigma stained dark.

Figure 13.- Alloy 20 containing 4.2 percent nickel, 31.3 percent cobalt, and 64.5 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1; X500. Sigma stained dark, epsilon with incompletely resolved sigma precipitate.

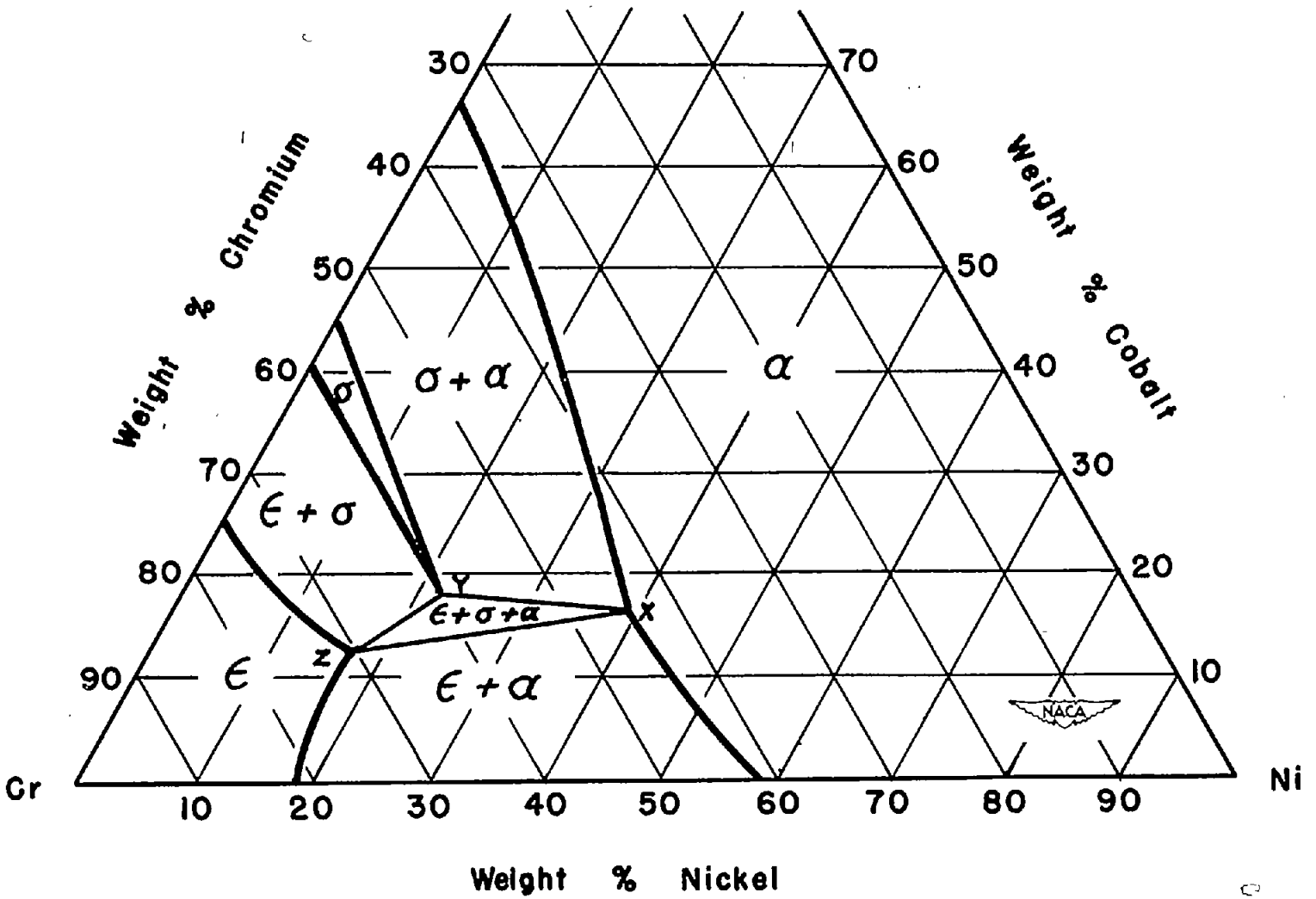

Figure 14.- 1200° C isothermal section of the chromium-cobalt-nickel ternary diagram.

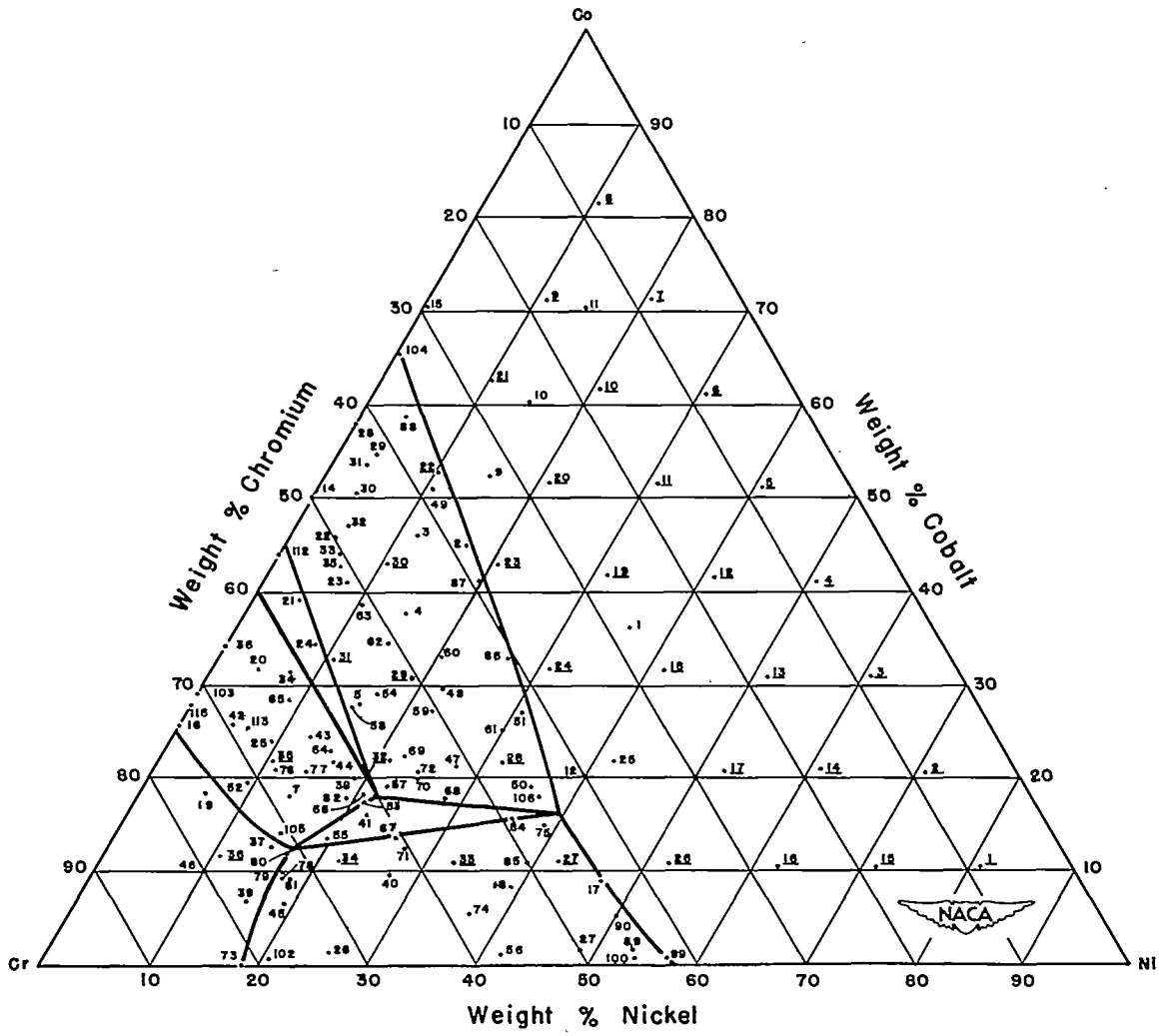

Figure 15.- Composition of alloys studied. Alloys obtained from the General Electric Co. are indicated by underlining of the corresponding number.

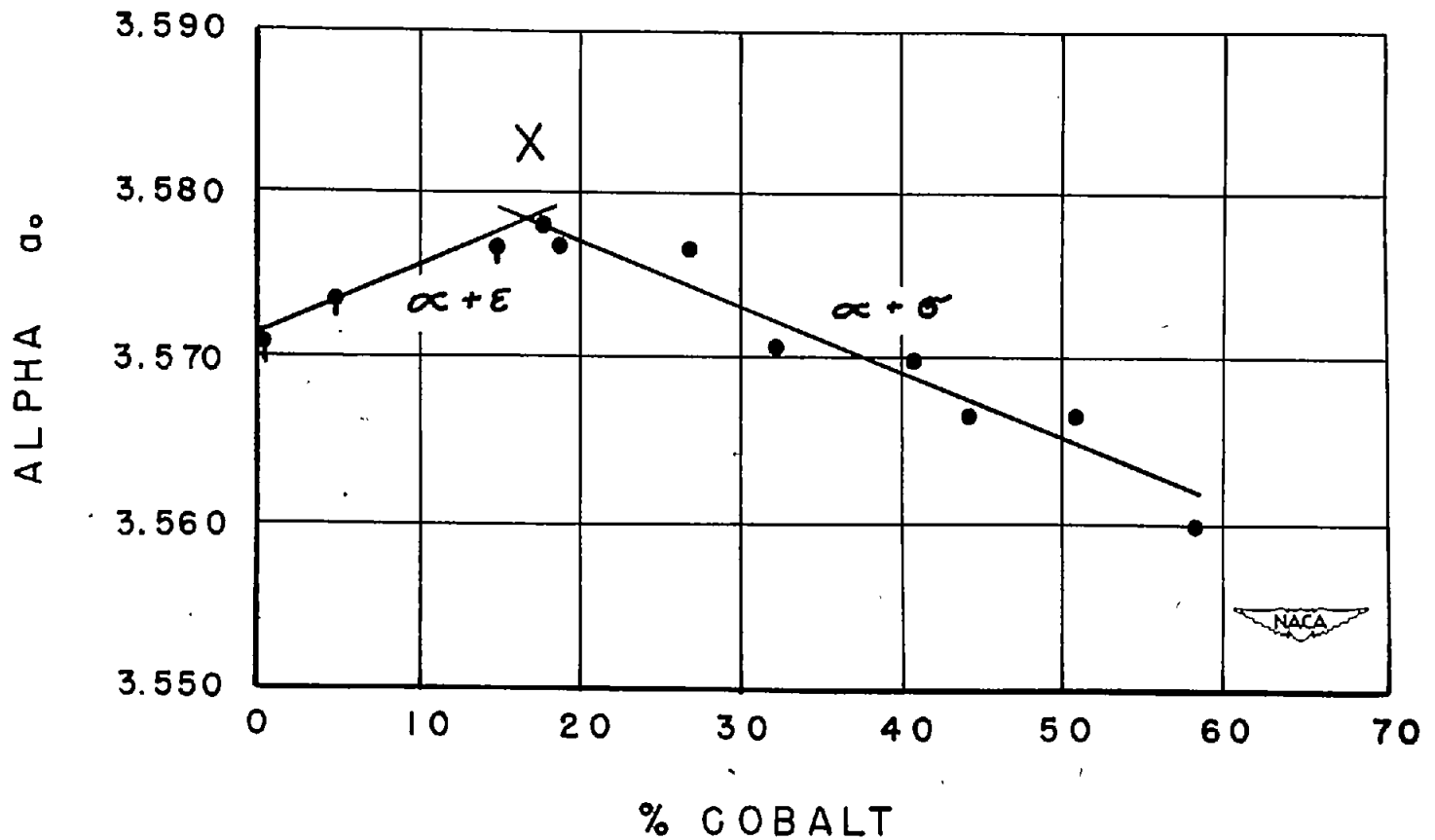

Figure 16.- Values of a_o of saturated alpha alloys plotted as function of cobalt content.

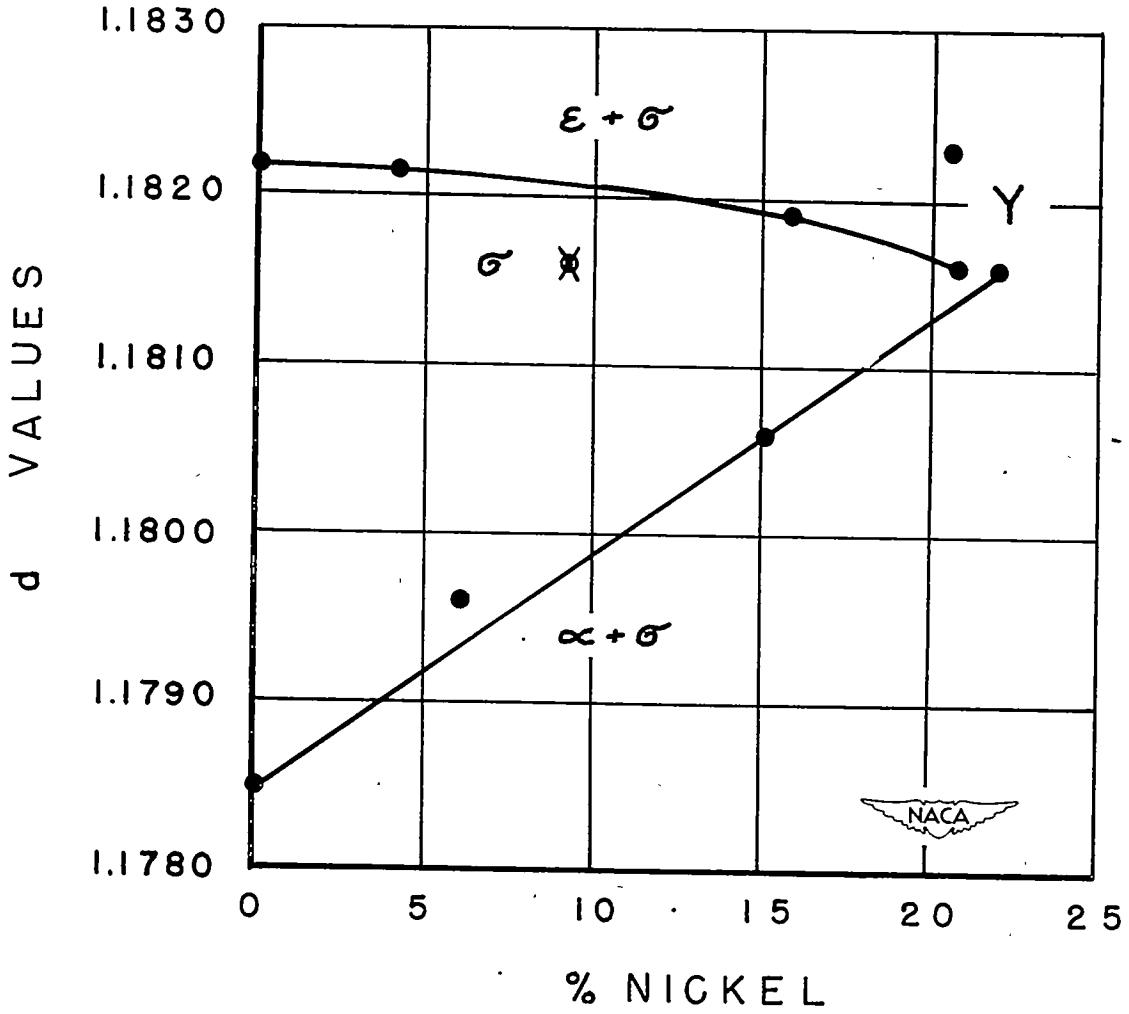

Figure 17.- Values of d for twenty-seventh line of sigma phase plotted as function of nickel content. Upper line refers to sigma phase saturated with epsilon and lower, to sigma saturated with alpha.

Figure 18.- Alloy 105 containing 15.4 percent nickel, 13.5 percent cobalt, and 71.1 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1; X500. Chromium-oxide inclusion in matrix of epsilon and sigma phases.

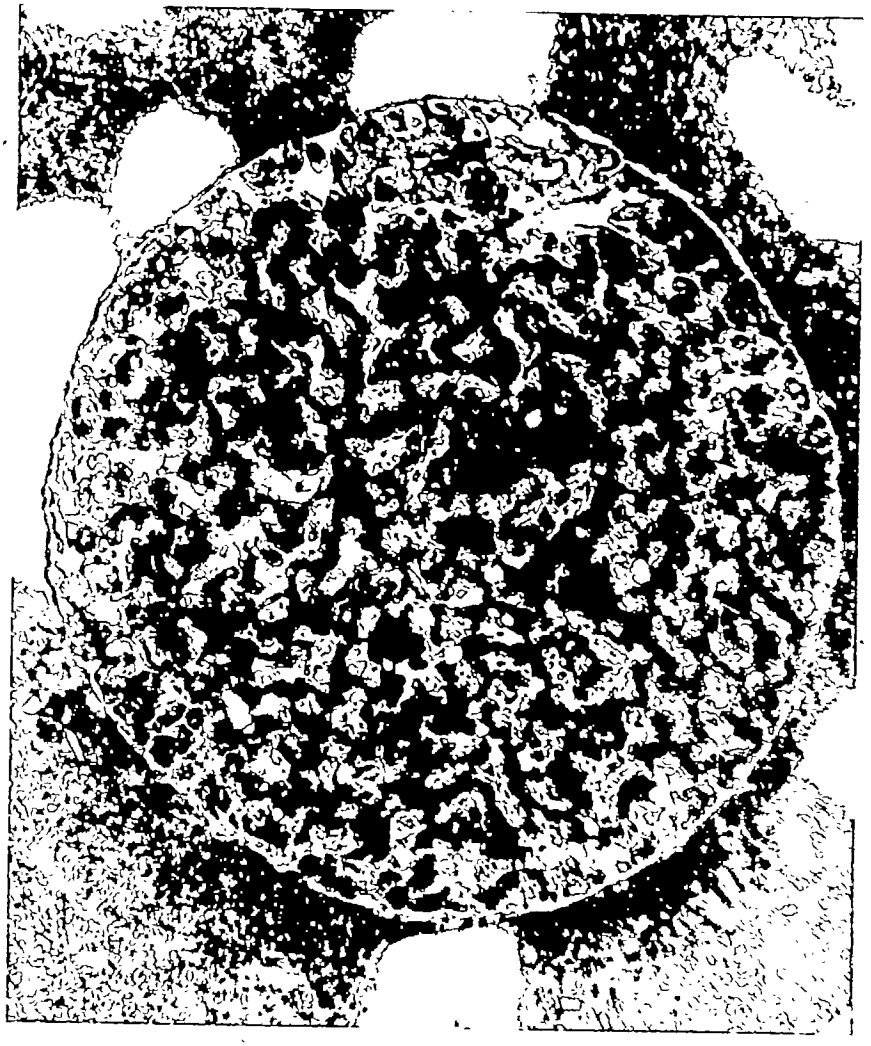

Figure 19.- Alloy 67 containing 26 percent nickel, 12.6 percent cobalt, and 61.4 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1; X500. Large drop-shaped slag inclusion.

Figure 20.- Alloy 74 containing 36.8 percent nickel, 5.1 percent cobalt, and 58.1 percent chromium. Homogenized at 1200° C for 12 hours; water-quenched; etch 1 without alkaline permanganate stain; X2500. Same as figure 10 except at higher magnification and still precipitate in epsilon is not completely resolved.

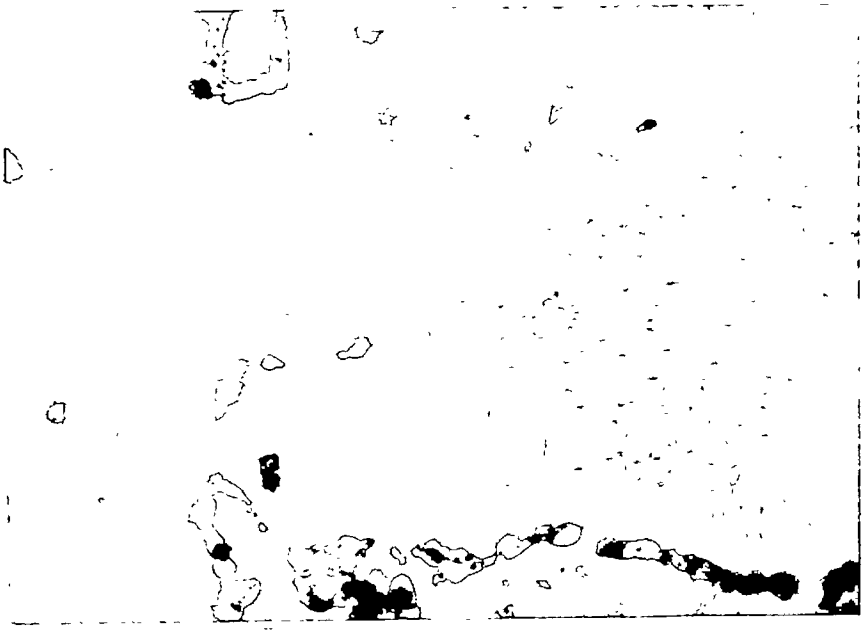

Figure 21.- Alloy 45 containing 19.1 percent nickel, 6.4 percent cobalt, and 74.5 percent chromium. Specimen from bottom of ingot slowly cooled from 1200° C, then homogenized at 1200° C for 12 hours, and water-quenched; etch 1 without alkaline permanganate stain; X500. Unknown white phase is usually found associated with chromium-oxide particles; matrix is epsilon phase with sigma-phase platelike precipitate.

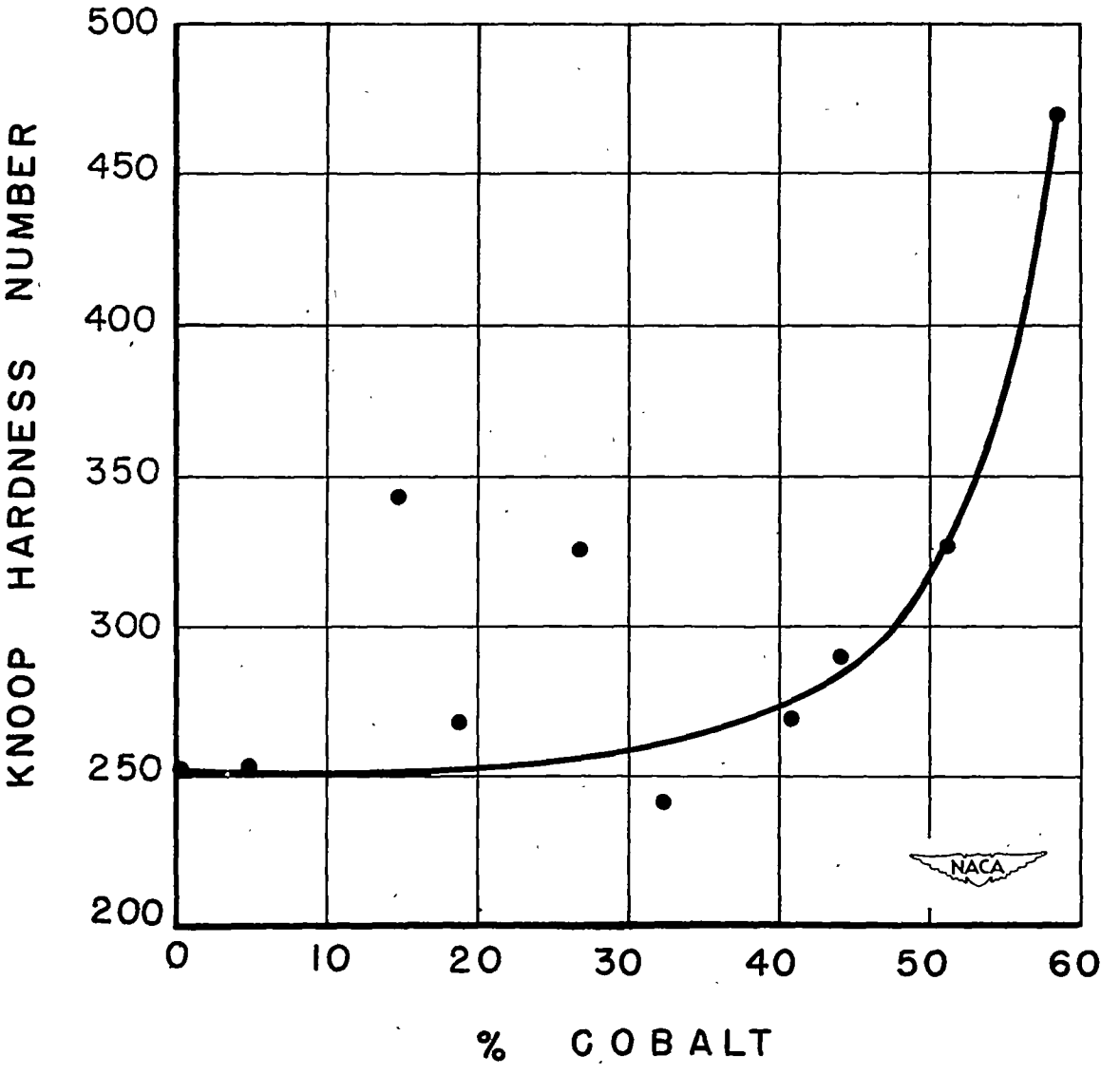

Figure 22.- Microhardness of saturated alpha phase of alpha boundary alloys plotted against cobalt content.

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