

REPORT 1122

SURVEY OF PORTIONS OF THE CHROMIUM-COBALT-NICKEL-MOLYBDENUM QUATERNARY SYSTEM AT 1,200° C¹

By SHELDON PAUL RIDEOUT and PAUL A. BECK

SUMMARY

A survey was made of portions of the chromium-cobalt-nickel-molybdenum quaternary system at 1,200° C by means of microscopic and X-ray diffraction studies. Since the face-centered cubic (alpha) solid solutions form the matrix of almost all practically useful high-temperature alloys, the solid solubility limits of the quaternary alpha phase were determined up to 20 percent molybdenum. The component cobalt-nickel-molybdenum, chromium-cobalt-molybdenum, and chromium-nickel-molybdenum ternary systems were also studied. The survey of these systems was confined to the determination of the boundaries of the face-centered cubic (alpha) solid solutions and of the phases coexisting with alpha at 1,200° C.

INTRODUCTION

In the development of technologically useful alloys it is usually of considerable help if the phase relationships and solid solubility limits are known. At the Metallurgy Department of the University of Notre Dame a project has been in progress for some years to determine the phase relationships in alloy systems involving chromium, cobalt, nickel, iron, and molybdenum, the transition elements of greatest importance in high-temperature alloys.

The determination of phase diagrams for systems of four or more components is an extremely laborious task. The problem must be approached in a systematic manner in order to avoid becoming hopelessly lost. The best method of attack is to begin by establishing the phase relationships in systems of two or three components and then continue by adding one new element at a time. The problem of presenting quantitative phase relationships diagrammatically for systems of three or more components necessitates holding one or more thermodynamic variables constant. For example, a ternary phase diagram may be presented as a series of isothermal sections or as a series of sections in each of which the amount of one component is held constant. For a quaternary system it is necessary to hold both temperature and the amount of one component constant in order to obtain two-dimensional diagrams. The temperature 1,200° C was chosen as that at which an initial isothermal survey could be most profitably made. This temperature is of immediate interest because it lies within the range of solution treatment for most high-temperature alloys now in use and also because here diffusion rates are fast enough to allow equilibrium conditions to be approached in reasonably short annealing periods. At lower temperatures, such as 800° C. the determination of these phase diagrams within extensive

composition ranges would be too time-consuming and therefore expensive. Work of this kind is planned only for limited important composition ranges.

Thus far two reports have been issued covering work done on this project. In the first report (reference 1) the 1,200° C isothermal section of the chromium-cobalt-nickel ternary system was presented. The second report (reference 2) gave a survey of the chromium-cobalt-nickel-iron quaternary system at 1,200° C in the composition ranges near the face-centered cubic solid-solution phase. This report also presented a study of some features of the chromium-cobalt-nickel and the chromium-cobalt-iron ternary systems at lower temperatures.

The present report presents a survey of portions of the chromium-cobalt-nickel-molybdenum quaternary system at 1,200° C. The face-centered cubic (alpha) solid solutions have, by far, the greatest practical importance in high-temperature alloys. For this reason the solid solubility limits of the quaternary alpha phase were determined up to 20 percent molybdenum.

It was also necessary to investigate the component cobaltnickel-molybdenum, chromium-cobalt-molybdenum, and chromium-nickel-molybdenum ternary systems, since these systems had not been adequately explored by previous investigators. (See "Literature Survey" for discussion of previous studies of the binary and ternary systems comprising the chromium-cobalt-nickel-molybdenum quaternary system.)

At the beginning of this work it became apparent that a definite and consistent nomenclature for phase designation would have to be adopted in order to avoid confusion and contradiction. For example, the iron-chromium sigma phase is isomorphous with the chromium-cobalt gamma phase and the iron-molybdenum zeta phase. In order to avoid contradiction in ternary and quaternary systems of these elements, where the isomorphous phases form uninterrupted solid solutions, it was decided to give all these phases the same designation. The designation sigma phase was selected as one most generally associated with this particular structure. Since this work began with a nonferrous system, the facecentered cubic solid solutions in the systems involving chromium, cobalt, nickel, and molybdenum have all been designated as alpha phase. For the sake of consistency this nomenclature was extended even to the chromium-cobaltnickel-iron quaternary system, although this phase in ferrous systems has been customarily referred to as gamma. On the other hand, the body-centered cubic solid solutions, which are usually named alpha in ferrous systems, are here referred

¹ Supersedes NACA TN 2683, "Survey of Portions of the Chromium-Cobalt-Nickel-Molybdenum Quaternary System at 1200° C" by Sheldon Paul Rideout and Paul A. Beck, 1952



to as epsilon phase in conformity with the nomenclature used for the chromium-rich alloys in the chromium-cobalt binary system. In the cobalt-molybdenum binary system the intermediate phase which coexists with alpha at 1,200° C has been earlier designated as epsilon. In the present investigation this phase was renamed mu since, as stated above, epsilon had already been used to designate the chromium-rich body-centered cubic phase. The hitherto unknown ternary phases discovered in the 1,200° C isothermal sections of the chromium-cobalt-molybdenum and the chromium-nickel-molybdenum ternary systems have been named R and P, respectively.

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 some of the work relating to the chromium-cobalt-molybdenum and chromium-nickel-molybdenum systems. The assistance of Messrs. C. Patrick Sullivan and Robert Hochman is also appreciated.

LITERATURE SURVEY

The chromium-cobalt-nickel-molybdenum quaternary systems comprises the following six binary and four ternary systems: Chromium-cobalt, chromium-nickel, cobalt-nickel, chromium-molybdenum, cobalt-molybdenum, nickel-molybdenum, chromium-cobalt-nickel, chromium-cobalt-molybdenum, chromium-nickel-molybdenum, and cobalt-nickel-molybdenum. All of the above binary systems were investigated previously. The chromium-cobalt system was investigated by Elsea, Westerman, and Manning (reference 3), and the most recent chromium-nickel phase diagram was reported by Jenkins, Bucknall, Austin, and Mellor (reference 4). The "Metals Handbook" (reference 5) gives the accepted cobalt-nickel diagram, which was thoroughly investigated by several workers.

The chromium-molybdenum binary system is also given in the "Metals Handbook" (reference 5). In recent work on molybdenum-rich alloys Kessler and Hansen (reference 6) confirm the results of other investigators that chromium and molybdenum are completely soluble in the solid state. The cobalt-molybdenum binary system was investigated by Sykes and Graff (reference 7). The transformation from face-centered cubic to hexagonal in pure cobalt above 1,000° C indicated in their diagram was not found by several later investigators (references 8 to 10). Henglein and Kohsok (reference 11) recently pointed out that the cobaltmolybdenum intermediate phase Co₇Mo₆ is isomorphous with the iron-molybdenum, cobalt-tungsten, and irontungsten intermediate phases Fe7Mo8, Co7W8, and Fe7W8. The crystal structure of the Co₇Mo₆ phase can be described as hexagonal or rhombohedral (reference 11). The nickelmolybdenum binary system, as determined by Ellinger, is given in reference 5.

Of the four ternary systems involved in the chromium-cobalt-nickel-molybdenum quaternary system, two were previously investigated. The 1,200° C isothermal section of the chromium-cobalt-nickel ternary system was investi-

gated by Manly and Beck (reference 1). This diagram was slightly modified in the chromium-cobalt sigma-phase-field region by Kamen and Beck (reference 2). Siedschlag (reference 12) investigated the chromium-nickel-molybdenum ternary system, but the results of that investigation proved to be of no help in the present work. The nickel-rich alloys were examined from a technological point of view only, and phase relationships were not studied in detail. It was, therefore, necessary to investigate the three ternary systems chromium-cobalt-molybdenum, chromium-nickel-molybdenum, and cobalt-nickel-molybdenum. The survey of these systems was confined to the determination of the boundaries of the face-centered cubic (alpha) solid solutions and of the phases coexisting with the alpha phase at 1,200° C.

The brittle intermetallic sigma phase, which occurs in many systems involving the transition elements, has recently become the subject of much interest and investigation. Sully and Heal (reference 13) have pointed out that the ironchromium sigma phase and the chromium-cobalt gamma phase are isomorphous, and Goldschmidt (reference 14) found that the iron-molybdenum zeta phase is also isomorphous with the iron-chromium sigma phase. Beck and Manly (reference 15) investigated the chromium-cobalt-iron and the chromium-cobalt-nickel ternary systems. They proved that the iron-chromium sigma phase and the chromium-cobalt gamma phase form an uninterrupted series of solid solutions across the chromium-cobalt-iron ternary isothermal section at 800° C. They also found that the chromium-cobalt gamma phase extends deep into the chromium-cobalt-nickel ternary system at 1,200° C in a manner suggesting that nickel atoms and cobalt atoms substitute for each other in forming the sigma phase, while the chromium content of the phase remains essentially unchanged. On the basis of these results and of the existence of the sigma phase in the iron-vanadium system, Beck and Manly (reference 15) suggested that the sigma phase should also occur in the cobalt-vanadium and the nickel-vanadium systems. Indeed, this was confirmed by Duwez and Baen (reference 16) who also formally postulated the criterion that a face-centered and a body-centered cubic metal are required in an alloy system before the sigma phase will form. In the present investigation special attention was given to the occurrence of the sigma phase, and further confirmation was obtained for the earlier observation that atoms of elements of like structure can substitute for each other in the formation of the sigma phase. A criterion for the formation of the sigma lattice in terms of electron vacancy concentration in the 3d sub-band was derived in order to rationalize the above observations.

EXPERIMENTAL PROCEDURE

In this work the phase boundaries were established by microscopic examination of carefully homogenized alloys. The phases were identified by means of X-ray diffraction. Details relating to the equipment used and to the melting and homogenizing procedures followed throughout the work were reported by Manly and Beck (reference 1). Molyb-

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denum in the form of a %-inch-diameter rod was used to make up the alloys. The lot analyses of the electrolytic chromium, of the cobalt rondelles, and of the nickel used are given in table I.

Most of the alloys were melted in Alundum crucibles, except for 34 alloys melted in zirconia and stabilized zirconia crucibles at the beginning of the work. The type of crucible used to melt each alloy is listed in table II. Early in the work it was found that molybdenum-bearing alloys were susceptible to zirconium pickup. This was confirmed by semiquantitative spectrographic analysis. The use of zirconia and stabilized zirconia crucibles was, therefore, discontinued, and all subsequent alloys were melted in Alundum crucibles. The zirconium pickup is treated in greater detail under "Discussion."

The ingots were generally found to be free of excessive segregation, except in a few isolated cases discussed later. Specimens for homogenization and subsequent microscopic and X-ray analysis were taken from the bottom section of each ingot. Immediately adjacent examples were used for chemical analysis. All specimens which consisted mainly of the face-centered cubic (alpha) solid solution were doubleforged prior to homogenization. This double-forging treatment consisted of heating the specimen at 1.200° C for \(\for \) hour, forging, reheating at 1,200 C for 1/2 hour, and forging again. With this preliminary treatment alpha alloys were easily homogenized by annealing at 1,200° C for 48 hours. Alpha alloys containing more than about 20 percent of any second phase were too brittle to be forged. Specimens from such allows were homogenized for 95 to 150 hours at 1.200° C. All specimens were quenched directly into cold tap water. It is very important that the oxygen be removed from the furnace atmosphere in which alloys containing molybdenum are being annealed, because of the extremely rapid rate of oxidation of these alloys at high temperatures. It is believed that the homogenizing treatments used gave very nearly equilibrium conditions, except in a few cases to be discussed later, because continued annealing, which in some cases was extended up to 200 hours, resulted in no detectable further changes in the microstructures.

After homogenization a powder for X-ray analysis was taken from each specimen, by either filing or crushing, depending on the brittleness of the alloy, and the remaining piece was prepared for microscopic examination to detect the presence or absence of a second phase. The phase boundaries were thus determined by the disappearing phase method.

It was found necessary to vary the etching procedure considerably, according to the composition of the alloy.

(1) The following etchants were used successfully to differentiate between the various phases:

Hydrochloric acid, milliliters	8.0
	0. 5
Glycerin, milliliters	2.0
Cupric chloride, milligrams 50 to	

The freshly polished specimen was either immersed in the etchant for several minutes, or, for more rapid attack,

swabbed with cotton saturated with the etchant. This etchant was used only to reveal the structure of the alpha phase; grain boundaries, annealing twins, and transformation striations became apparent, and any second-phase particles present were clearly delineated. It was not possible, however, to identify which second phase was present by using this etchant alone.

(2) The following electrolytic etching and staining procedure was used with alloys in the chromium-nickel-molybdenum ternary system:

Oxalic acid, grams	8
Distilled water, milliliters	92
CathodeStain	less steel
Voltage, volts (d-c.)	6
Electrode spacing, inch.	1
Temperature, °C	20 to 30
Time, seconds	8 to 10

The specimen was removed from the etching bath and immediately immersed for 10 to 20 seconds into a staining solution consisting of 5 grams of potassium permanganate and 5 grams of sodium hydroxide dissolved in 90 milliliters of distilled water. This etching and staining method worked well with the epsilon phase. Grain boundaries became evident and the characteristic Widmanstätten precipitate of sigma in the epsilon phase, when present, became clearly recognizable. The epsilon phase was stained a very light tan color, or a darker brown when the Widmanstätten precipitate was present. The alpha phase always remained unattacked and unstained. The chromium-nickel-molybdenum ternary sigma phase always stained, and a faint structure was sometimes brought out in this phase. The color of the stain on the sigma phase varied from bright green or red to purple. The grain boundaries of the ternary P phase were attacked and this phase, too, was always stained, the color varying from green to red and orange. The delta phase was generally very unevenly attacked and either did not stain or stained an uneven brownish color. Grain boundaries were revealed in the delta phase. With chromium-nickel-molybdenum alloys great success was experienced in differentiating between epsilon, sigma, and alpha when these phases coexisted. As a result of this, it was possible to locate the corner of the three-phase alpha-plus-epsilon-plus-sigma field on the alpha boundary by metallographic means. Even when present as small particles in an alpha matrix, sigma consistently stained a brilliant color, whereas the epsilon phase never stained more than a light tan color. It was difficult to distinguish between minor amounts of the sigma and the P phases in an alpha matrix because of their similar staining characteristics. However, when sigma and P were adjacent in the same alloy, it was possible to distinguish one phase from the other. Final identification, of course, was made by means of X-ray analysis.

(3) The electrolytic oxalic-acid etchant described above proved unsatisfactory for chromium-cobalt-molybdenum alloys. The following electrolytic etchant, used in conjunction with the previously described staining solution, was used with satisfactory results:

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Concentrated phosphoric acid, milliliters.	
Distilled water, milliliters	95
Cathode	
Voltage, volts (d-c.)	6
Electrode spacing, inch.	
Temperature, °C	20 to 30
Time, seconds	10 to 15

The alpha phase was lightly attacked but remained unstained. The sigma phase was lightly attacked and stained colors varying from orange to blue or purple. A fine Widmanstätten precipitate was sometimes observed in the sigma phase. The chromium-cobalt-molybdenum ternary R phase was unattacked, but this phase stained yellow to rusty brown. The mu phase was attacked and usually stained pale blue or did not stain at all. Grain boundaries and tiny annealing twins were observed in the mu phase. Sigma, R, and alpha were easily distinguished from each other when these phases occurred together in the same alloy, but small particles of sigma were indistinguishable from small particles of either the R or the mu phase in an alpha matrix. The mu phase was readily differentiated from R.

(4) It was necessary to decrease the acidity of the phosphoric-acid electrolyte and increase the alkalinity of the alkaline permanganate staining solution in order to differentiate successfully between the delta and the mu phases in cobalt-nickel-molybdenum alloys. The following solution was used:

Concentrated phosphoric acid, milliliters	2. 5
Distilled water, milliliters	97. 5

Etching conditions were the same as those for procedure 3. . The specimen was then immersed into a staining solution containing 20 grams of sodium hydroxide and 5 grams of potassium permanganate dissolved in 75 milliliters of distilled water. The alpha phase was lightly attacked but remained unstained. The delta phase was unevenly attacked, grain boundaries being revealed, and was stained dark green or blue. The mu phase was more evenly attacked; grain boundaries and occasional twins were evident. The mu phase stained a number of different colors, apparently depending upon the orientation, each grain or twin showing only one color. With this etching procedure it was possible to detect small amounts of the mu phase in a matrix of delta but, because of the wide variation of color from grain to grain in the mu phase, it was not possible to identify small amounts of delta in a matrix of the mu phase. This difficulty of microscopically identifying small amounts of the delta phase in a matrix of mu was circumvented by the use of an X-ray method to determine the solubility limit of nickel in the mu phase. In a plot of the d values for one high-angle diffraction line in a series of mu alloys as a function of the nickel content, the solubility limit is indicated where the slope of the curve becomes zero.

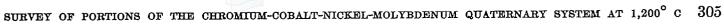
The powders for X-ray analysis were sealed under vacuum in fused-quartz capsules and annealed at 1,200° C for ½ hour. The capsules were then quenched directly into cold tap water. The powders were mounted on 1- by 1-inch cards with a colloidal glue, and a diffraction pattern was taken in an asymmetrical focusing camera of 20-centimeter diameter,

using unfiltered chromium radiation at 8 milliamperes and 30 kilovolts. Thus, the identity of the phases present in each homogenized allow was confirmed by X-ray diffraction. However, the X-ray method of identification was found relatively insensitive to small amounts of a second phase, especially in alloys having an alpha matrix. This difficulty was surmounted partially by careful preparation of the powder. A large quantity of filings was collected from the specimen to insure obtaining a representative sample. minor phase was generally much more brittle than the alpha matrix and had a much smaller particle size. It was concentrated by sieving the powder to 200 mesh. Only the finest powder from the sample was used to prepare the X-ray specimen. In handling this fine powder precautions were necessary in order to avoid losing any of the minor phase. For example, the original filings had to be collected on a smooth tracing paper or Celluloid, to which the powder will not adhere and from which the fine powder may be easily recovered.

An X-ray method of locating three-phase-field corners on the alpha phase boundary, as described previously by Manly and Beck (reference 1), was used in this work to supplement the microscopic results. The method consists of plotting the lattice parameters of the saturated alpha alloys as a function of composition. The three-phase-field corner is usually indicated by a rather sharp change in the slope of the curve. The lattice parameters for these plots were determined by taking back-reflection diffraction patterns from the surface of microspecimens known to be saturated alpha. Flat film and a collimating system of 1-millimeter diameter were used. By using unfiltered chromium radiation and a specimen-to-film distance of 29.54 millimeters, the chromium $K\alpha$ reflections from the (220) planes and the chromium $K\beta$ reflections from the (311) planes of the alpha phase were recorded. Smooth circles were obtained by rotating the specimen about an axis parallel to that of the collimating system but offset from it. The lattice parameter determined from each of these lines was plotted against $\cos^2\theta(2\cos^2\theta-1)$ and extrapolated to $\theta=90^{\circ}$ in order to eliminate systematic errors.

EXPERIMENTAL RESULTS

The experimental data for all alloys investigated are given in tables III to VI. The 1,200° C isothermal sections for the cobalt-nickel-molybdenum, chromium-cobalt-molybdenum, and chromium-nickel-molybdenum ternary systems and the solubility limits of the alpha phase in the 2.5-, 5-, 10-, and 20-percent-molybdenum quaternary sections, as shown in figures 1 to 8, were drawn in accordance with these data. The amount of each phase, as estimated microscopically in the homogenized structure, is tabulated together with corresponding X-ray diffraction data for each alloy. The amounts of the phases, corresponding to the phase diagrams, are also given for comparison. For alloys which were chemically analyzed the content in acid insoluble material was determined and found to vary from nil to a few tenths of 1 percent. The compositions of chemically analyzed alloys reported in the tables were corrected to 100-percent-metal content.



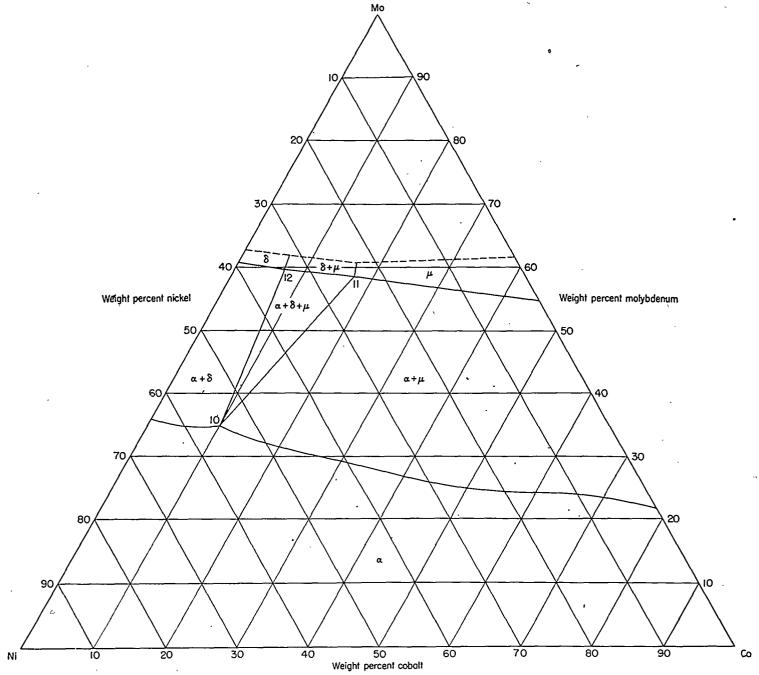
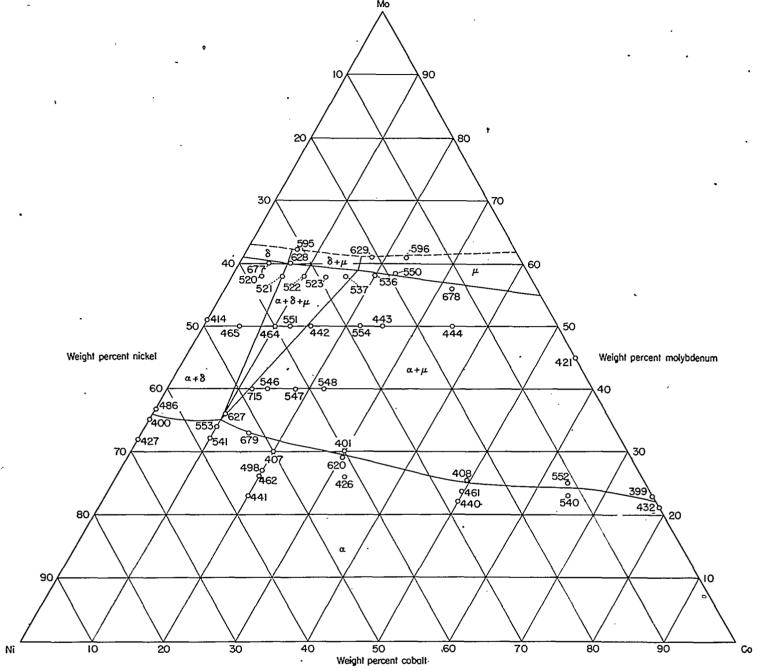


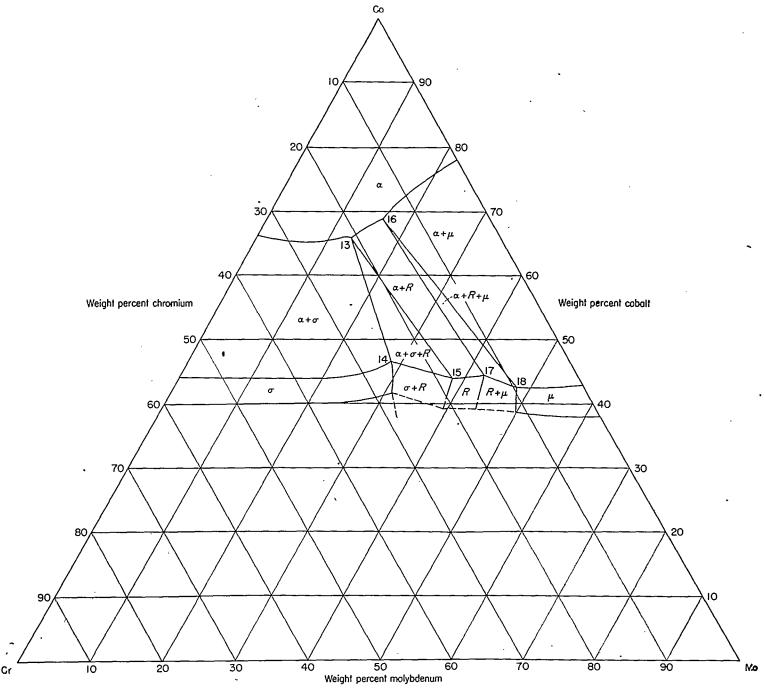
Figure 1.--The 1,200° C isothermal section of cobalt-nickel-molybdenum ternary system.

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 $\textbf{FIGURE 2.} \textbf{-The 1,200} \ \textbf{C} \ \textbf{ isothermal section of cobalt-nickel-molybdenum ternary system with alloy compositions indicated. } \\$

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 ${\tt F_{IGURE~3.--The~1,200°~C~isothermal~section~of~chromium-cobalt-molybdenum~ternary~system.}$

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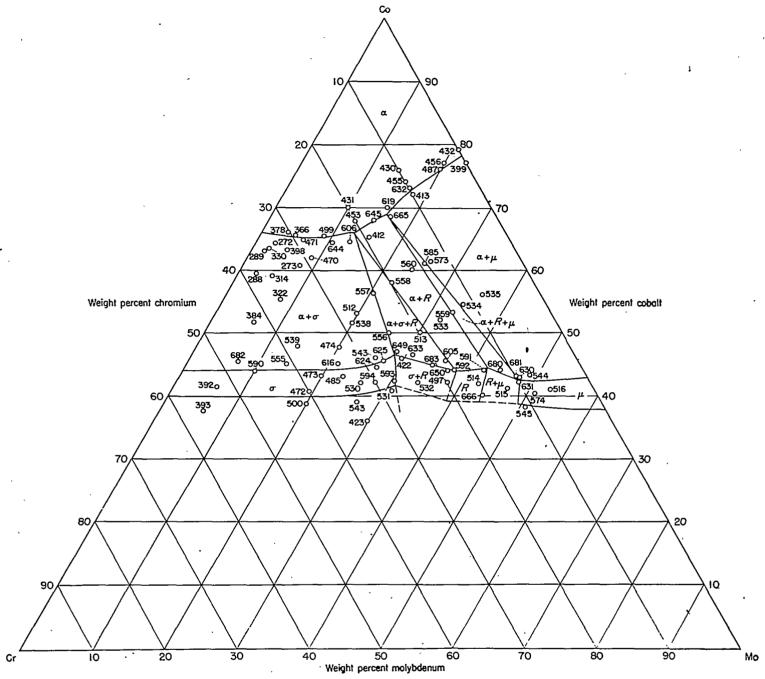


FIGURE 4.—The 1,200° C isothermal section of chromium-cobalt-molybdenum ternary system with alloy compositions indicated.

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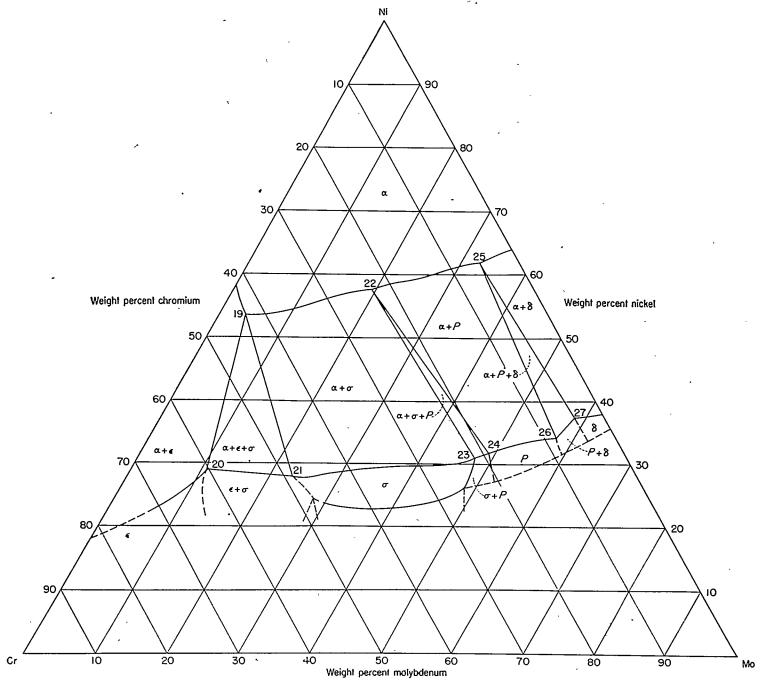
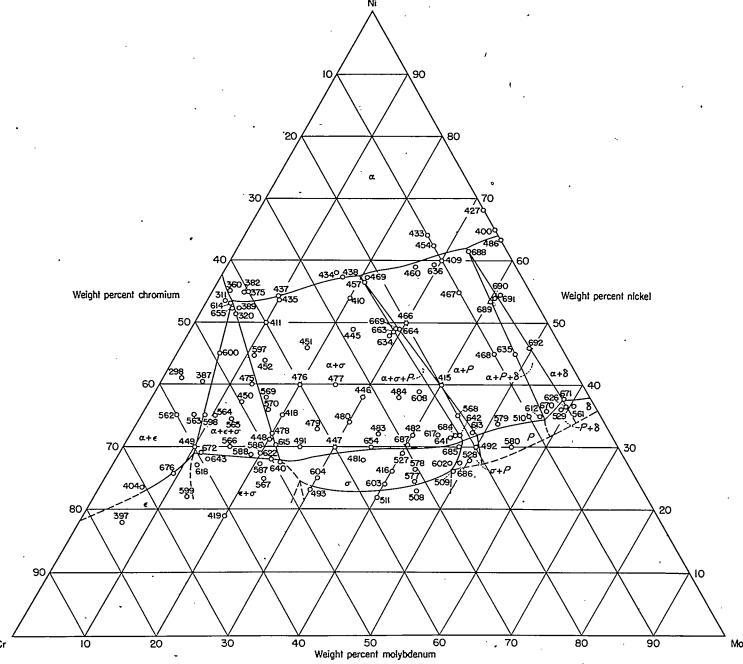


Figure 5.—The 1,200° C isothermal section of chromium-nickel-molybdenum ternary system.

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 $\textbf{Figure 6.--The 1,} 200^{\circ} \ O \ \textbf{isothermal section of chromium-nickel-molybdenum ternary system with alloy compositions indicated.}$

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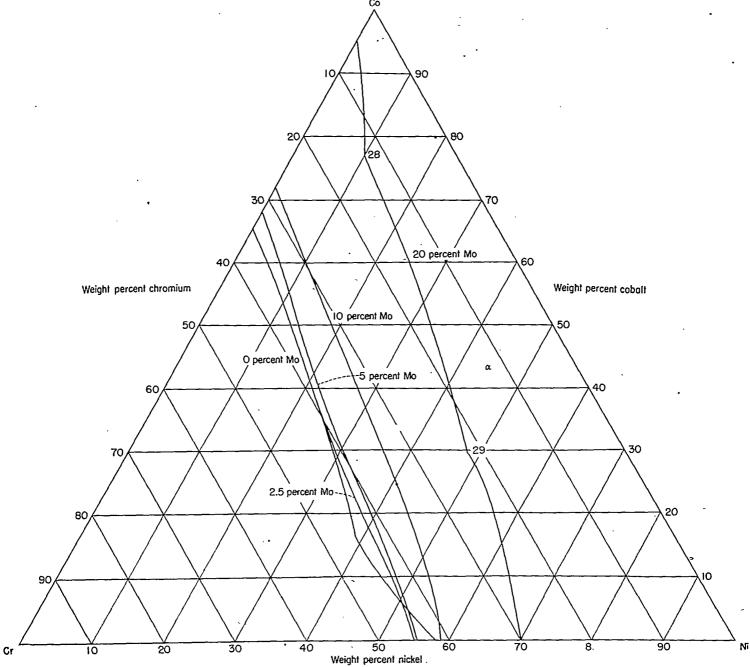


FIGURE 7.—Alpha-phase-field boundary at 1,200° C in chromium-cobalt-nickel-molybdenum quaternary system for constant molybdenum contents of 2.5, 5, 10, and 20 percent

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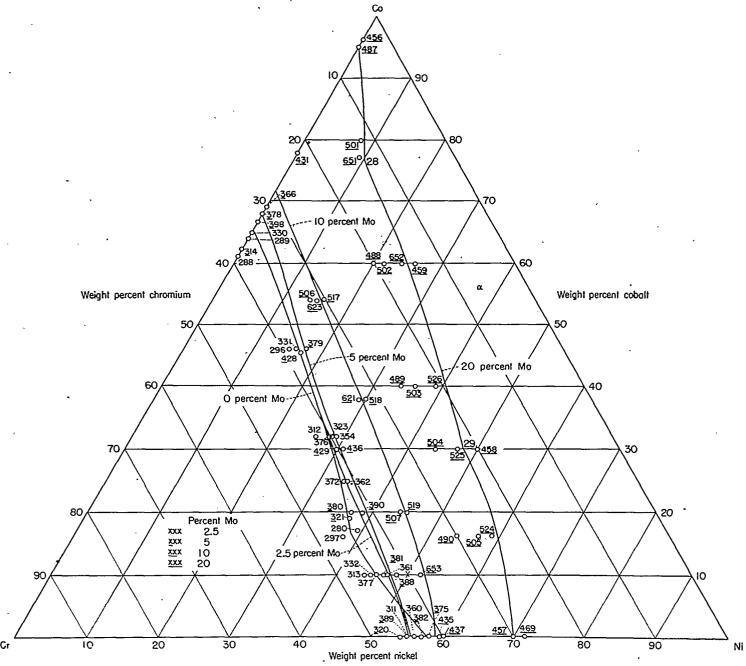


FIGURE 8.—Alpha phase-field boundary at 1,200° C in chromium-cobalt-nickel-molybdenum quaternary system for constant molybdenum contents of 2.5, 5, 10, and 20 percent with alloy compositions indicated.

PHASES '

The various phases identified in this investigation and the metallographic characteristics of each phase are described in the following paragraphs.

Alpha.—The alpha phase, which forms the matrix of most of the practically important high-temperature alloys, is based on solid solutions of the face-centered cubic elements cobalt and nickel. This phase, being relatively soft and ductile, was easily hot-forged, and alpha alloys rich in nickel could be cold-worked to some extent. Reagent 1 was used to reveal the microstructure of the alpha phase. The structure is typical of most face-centered cubic solid solutions, showing equiaxed grains and numerous annealing twins. In alpha alloys containing small amounts of a second phase a great grain-size contrast was sometimes seen. Such "duplex" structures undoubtedly occur as a result of the inhibition effect of small second-phase particles on grain growth (reference 17). Upon cooling, pure cobalt is known to transform from the face-centered cubic to the hexagonal close-packed structure by a martensitic transformation (reference 8). In cobalt-rich alpha solid solutions the beginning of this transformation is manifested in the microstructure by the presence of striations, as illustrated in figure 9. These transformation striations were also observed in saturated cobalt-molybdenum and cobalt-chromium alpha alloys and in quaternary alpha alloys rich in cobalt. Additions beyond about 15 percent nickel to cobalt-molybdenum and 30 percent nickel to cobalt-chromium saturated alpha alloys seem to suppress the transformation, as evidenced by the absence of striations in the microstructure.

Microspecimens of alloys containing alpha in addition to any other phases exhibited a pronounced relief effect in the as-polished and unetched condition. The relief is due to the large difference in hardness between alpha and the phases which coexist with it at 1,200° C. In unetched microspecimens the alpha phase had a slightly amber or yellowish

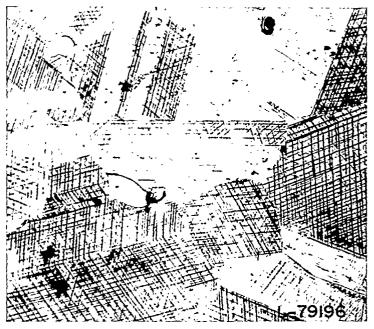


FIGURE 9.—Alloy 206 containing 38.02 percent chromium, 44.85 percent cobalt, 14.63 percent nickel, and 2.5 percent molybdenum. Etched according to procedure 1; small particles of second phase in an alpha matrix; transformation strictions revealed in alpha phase; X500.

tint, while the other phases appeared white. Figure 10 shows a banded structure which was observed in alloys consisting of approximately equal amounts of the alpha and mu phases. Figure 11 illustrates the general shape and distribution of minor amounts of alpha in a matrix of the sigma phase. This is typical of the distribution of minor amounts of alpha in all phases. Alloys which consisted of larger amounts of alpha coexisting with any of the other phases exhibited microstructures similar to the one shown in figure 12. Data from a typical X-ray diffraction pattern of the alpha phase are given in table VII. Evidence that preferred orientation may occur in forged and annealed alpha alloys was found in some of the back-reflection pictures taken from the surface of microspecimens.

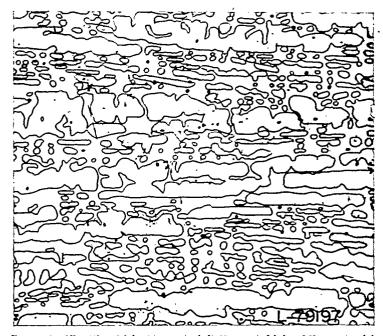


Figure 10.—Alloy 443 containing 25 percent cobait, 25 percent nickel, and 50 percent molybdenum. Etched according to procedure 4 but stain omitted; alpha phase arranged in banded dendritic pattern in matrix of mu phase; X250.

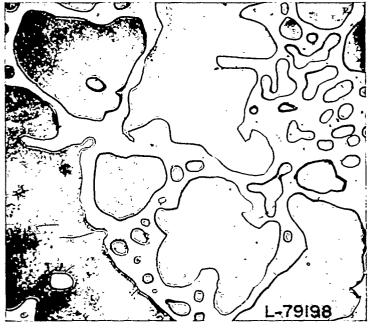


FIGURE 11.—Alloy 608 containing 23.5 percent chromium, 39 percent nickel, and 37.5 percent molybdenum. Etched and stained according to procedure 2; minor amounts of unstained alpha in matrix of stained sigma phase; X250.



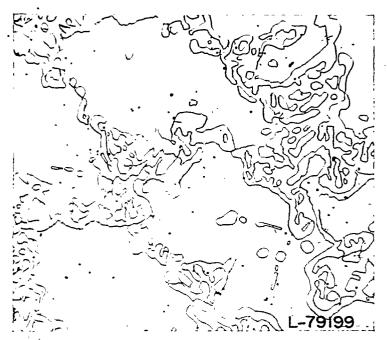


FIGURE 12—Alloy 467 containing 10 percent chromium, 55 percent nickel, and 35 percent molybdenum. Etched according to procedure 2 but stain omitted; typical distribution of minor amounts of P phase in matrix of alpha; X250.

Epsilon.—The body-centered cubic epsilon phase at 1,200° C is based on solid solutions of chromium and molybdenum. Within the composition ranges investigated in this work, the epsilon phase was encountered only in the chromiumnickel-molybdenum ternary isothermal section where it coexists with the alpha and sigma phases and in quaternary alloys containing less than about 3 percent molybdenum near the chromium-nickel side of the diagram, where it coexists with alpha. When etched and stained according to procedure 2, the microstructure of the epsilon phase was clearly revealed. This phase stained a light tan color and, in this work, a characteristic Widmanstätten type of precipitate was always observed in the large equiaxed grains of the epsilon phase, with the exception of epsilon coexisting with alpha in alloys near the chromium-nickel binary side of the diagram. This Widmanstätten precipitate was previously found in chromium-rich alloys in the epsilon phase fields of both the chromium-cobalt-nickel and the chromiumcobalt-iron ternary isothermal sections at 1,200° C (references 1 and 2) and was identified in both cases as being the sigma phase. In the present work, too, it has been concluded that the Widmanstätten precipitate consists of the sigma phase. /In epsilon alloys very near to the corner of the three-phase alpha-epsilon-sigma field in the chromiumnickel-molybdenum ternary isothermal section, the Widmanstätten precipitate in the epsilon phase is extremely heavy. (See fig. 13.) The epsilon phase was easily distinguished from alpha or sigma, either by the precipitate in epsilon or by its tan color, when stained (procedure 2), since the alpha, phase remains unstained and the sigma phase stains to a brilliant color. Figure 14 is an example of this. where the three phases are seen to coexist. This alloy was slightly deformed prior to microscopic examination. Note the severe cracks in the heavily stained sigma and the few cracks in the lightly stained epsilon. Table VIII gives the

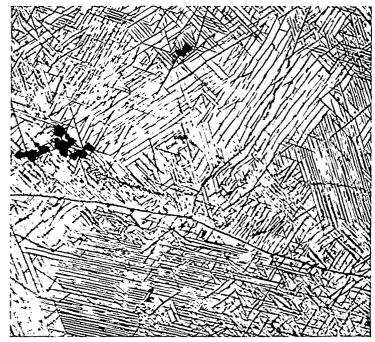


FIGURE 13.—Alloy 599 containing 65 percent chromium, 22 percent nickel, and 13 percent molybdenum. Etched and stained according to procedure 2; heavy Widmanstitten precipitate of sigma in epsilon phase; dark oxide inclusions and grain boundaries shown in epsilon phase; X500.



Figure 14.—Alloy 600 containing 48.5 percent chromium, 45.4 percent nickel, and 0.1 percent molybdenum. Etched and stained according to procedure 2; heavily stained and severely cracked particles of sigma plus lightly stained epsilon with few cracks in matrix of unstained alpha phase; X250.

data from a typical X-ray diffraction pattern of the epsilon phase.

Sigma.—The sigma phase is an extremely brittle intermetallic phase which, in this investigation, occurred in the 1,200° C isothermal sections of the chromium-cobalt-molybdenum and chromium-nickel-molybdenum ternary systems, as well as in chromium-cobalt-nickel-molybdenum quaternary alloys containing up to 20 percent molybdenum. The sigma phases in these, as in other systems, are isomorphous. Recent investigations on single crystals of the

chromium-cobalt and iron-chromium sigma phases have yielded information showing that the crystal class of sigma is tetragonal.2 Microspecimens from sigma alloys invariably showed cracks as a result of the brittleness of the phase. Qualitatively, ingots of chromium-nickel-molybdenum ternary sigma alloys did not seem to be quite so brittle as chromium-cobalt-molybdenum sigma alloys in that they did not shatter quite so easily. Ingots of chromium-cobaltmolybdenum sigma alloys were so brittle that they shattered when dropped to the floor. Etching and staining the chromium-nickel-molybdenum ternary sigma phase was accomplished by following procedure 2. Prolonged etching brought out faintly the grain boundaries in sigma, as shown in figure 15. It is interesting to note that, in specimens which consisted almost entirely of the sigma phase, the color of the stain on sigma was very light, whereas massive particles of sigma in a matrix of some other phase always stained a brilliant color. The reason for this is not clearly understood. In the two-phase sigma-plus-P field of the chromiumnickel-molybdenum system at 1,200° C, the grains of these two phases were very intimately arranged so that grain boundaries seemed to correspond to phase boundaries. This is illustrated in figure 16. The microstructure of chromium-cobalt-molybdenum alloys in which the sigma phase coexisted with minor amounts of the alpha or R phases was best revealed by etching and staining, as outlined in procedure 3. The grain boundaries of the sigma phase were not attacked, but a scattered Widmanstätten precipitate was sometimes brought out. (See fig. 17.) The identity of this precipitate is not known.

Sigma coexists with the alpha, epsilon, and R phases in randomly distributed particles and with the epsilon phase in some cases as a Widmanstätten precipitate. Small particles of the sigma phase which precipitated along the grain boundaries from a supersaturated chromium-cobalt-molybdenum alpha alloy are shown in figure 18. Etching procedure 3 was used; consequently, the structure of the alpha was not revealed. Data from typical X-ray diffraction patterns of the chromium-nickel-molybdenum and chromium-cobalt-molybdenum sigma phases are listed in table IX. It is seen from a comparison of the two patterns that these sigma phases are isomorphous.

Delta.—Solid solutions based on the nickel-molybdenum delta phase are formed in the 1,200° C isothermal sections of the chromium-nickel-molybdenum and cobalt-nickel-molybdenum ternary systems. The crystal structure of the delta phase is not known. This phase is hard and brittle, although not nearly so brittle as the sigma phase. Ingots of alloys consisting mainly of the delta phase could not be broken by a sharp blow with a hammer. Fine cracks were sometimes seen in the microstructure, which was revealed by etching procedure 4. These cracks probably originated during the preliminary grinding of the microspecimen. Figure 19 is a photomicrograph of an alloy of delta with minor amounts of alpha and mu. This specimen was etched and stained according to

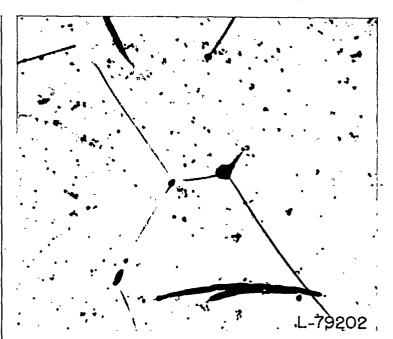


FIGURE 15.—Alloy 602 containing 25 percent chromium, 27.5 percent nickel, and 47.5 percent molybdenum. Etched and stained according to procedure 2; grain boundaries revealed in cracked matrix of sigma phase; X500.

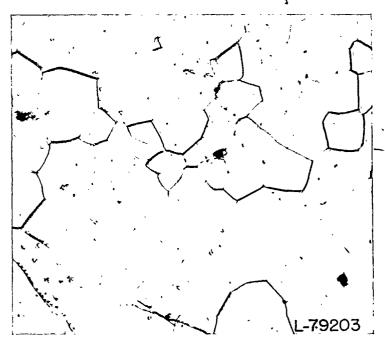


FIGURE 16.—Alloy 492 containing 20 percent chromium, 30 percent nickel, and 50 percent molybdenum. Etched and stained according to procedure 2; particles of sigma phase clearly delineated in matrix of P phase; grain boundaries revealed; X1,000.

procedure 4. Note the large grains of delta and the much smaller grains of mu which are stained to various colors and exhibit occasional tiny annealing twins. The alpha particles are slightly roughened but remained unstained and appear white. As the amount of the mu phase coexisting with delta increases, it becomes increasingly difficult to distinguish between the two phases. In chromium-nickel-molybdenum alloys consisting largely of delta, no difficulty was experienced in differentiating between the delta and P phases. Small particles of the P phase in a matrix of delta are shown in figure 20. Data from a typical X-ray diffraction pattern of the delta phase are listed in table X.

² Reference 18; also private communication from Drs. J. S. Kasper, B. F. Decker, and J. R. Belanger, General Electric Research Laboratory.





FIGURE 17.—Alloy 392 containing 52.6 percent chromium, 41.4 percent cobalt, and 6 percent molybdenum. Etched and stained according to procedure 3; scattered Widmanstatten precipitate in matrix of sigma phase; identity of precipitate unknown; X500.



FIGURE 18.—Alloy 471 containing 28.83 percent chromium, 64.8 percent cobait, and 6.37 percent molybdenum. Etched and stained according to procedure 3; small particles of stained sigma phase outlining grains of unstained alpha phase; X500.

Mu.—In the present work solid solutions based on the intermediate cobalt-molybdenum epsilon phase were renamed mu to avoid contradictions in the nomenclature. This phase occurs in the 1,200° C isothermal sections of the chromium-cobalt-molybdenum and cobalt-nickel-molybdenum ternary systems. The mu phase also coexists with alpha in chromium-cobalt-nickel-molybdenum quaternary alloys from at least 17 to 20 percent molybdenum near the cobalt-nickel side of the diagram. The crystal structure of the mu phase can be described as hexagonal or rhombohedral (reference 11). This phase is isomorphous with the corresponding intermediate phase in the iron-molybdenum; iron-tungsten, and cobalt-tungsten binary systems (reference 11). Ingots of mu alloys displayed

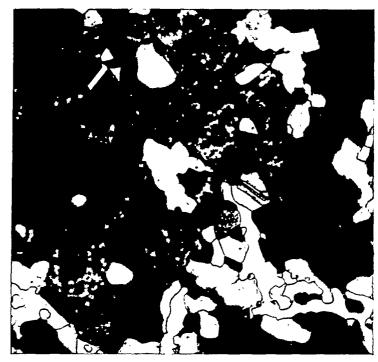


FIGURE 19.—Alloy 522 containing 10 percent cobalt, 32 percent nickel, and 58 percent molybdenum. Etched and stained according to procedure 4; minor amounts of unstained (white) alpha phase plus small grains of mu phase stained to various colors and showing occasional annealing twins in matrix of delta phase; delta phase unevenly attacked and heavily stained; X500.



FIGURE 20.—Alloy 626 containing 4 percent chromium, 35,5 percent nickel, and 59.5 percent molybdomum. Rtched and stained according to procedure 2; traces of P phase in matrix of delta; grain boundaries in delta phase very faintly visible; X1,500.

physical characteristics similar to those of ingots of delta alloys. A macrostructure was generally visible, without etching, on the surface of the ingot. The macrostructure was either granular or dendritic in nature. No relief effect was observed in as-polished and unetched microspecimens containing minor amounts of the delta or R phases in a matrix of mu, indicating that these phases have nearly the same hardness. In attempting to reveal clearly the microstructure of the mu phase it was found that large areas

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throughout the specimen were preferentially attacked, giving one the impression that the alloy contained two phases when actually there was only one. (This was proved repeatedly by careful X-ray diffraction studies.) After experimenting with various etching techniques, all with the same result, it was concluded that the preferential attack is an orientation effect. Figure 21 shows the structure of a typical mu alloy. This specimen was etched according to procedure 4 but the stain was omitted.

The mu phase coexists with the delta and R phases in randomly distributed particles. A banded structure in alloys of mu plus alpha has been discussed and illustrated previously in figure 10. Table XI gives the data from a typical X-ray diffraction pattern of the mu phase.

P phase.—The P phase was discovered in the 1,200° C isothermal section of the chromium-nickel-molybdenum ternary system. This phase is not known to occur in any of the three binary systems at any temperature. The crystal structure of the P phase was not determined. Alloys of P were hard and brittle, having much the same physical characteristics as alloys of the chromium-nickel-molybdenum ternary sigma phase. Numerous cracks were observed under the microscope, as in the case of the ternary sigma phase. Grain boundaries in the P phase were attacked when etched by procedure 2, and this etchant also produced stain colors varying from green to red and orange. Because of the similarity in microstructures and staining characteristics of the P and sigma phases, it was difficult to distinguish between them microscopically. In figure 22, minor amounts of sigma and P are seen in an alpha matrix. Sigma is stained darker than P, but the contrast is slight. Small particles of the delta or alpha phases could easily be identified in a matrix of the P phase. Data from a typical X-ray diffraction pattern of the P phase are given in table XII.



Figure 21.—Alloy 550 containing 22.74 percent cobalt, 18.77 percent nickel, and 58.49 percent molybdenum. Etched according to procedure 4 but stain omitted; structure of mu phase; preferential attack probably due to orientation effect; X500.

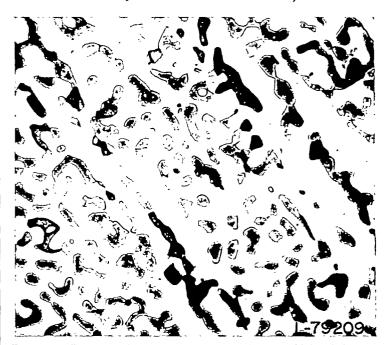


Figure 22.—Alloy 669 containing 22 percent chromium, 49 percent nickel, and 29 percent molybdenum. Etched and stained according to procedure 2; minor amounts of sigma and P phases (both stained) in unstained matrix of alpha phase; slight contrast between sigma and P particles; X500.

R phase.—The R phase was discovered in the 1,200° C isothermal section of the chromium-cobalt-molybdenum ternary system. The crystal structure of the R phase was not determined. Ingots of alloys which consisted of the R phase had about the same physical characteristics as delta and mu alloy ingots. When etched and stained according to procedure 3, the R phase was unattacked but stained yellow to rusty brown. Small quantities of the sigma, mu, or alpha phases in a matrix of R were easily identified microscopically. Figure 23 shows alpha and a few particles of the sigma phase in a matrix of the R phase. The sigma

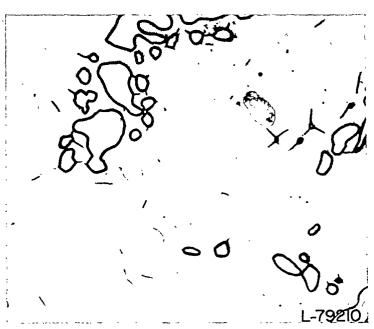


FIGURE 23.—Alloy 605 containing 18.5 percent chromium, 45.5 percent cobalt, and 36 percent molybdenum. Etched and stained according to procedure 3; small particles of stained sigma plus minor amounts of unstained (white) alpha phase in stained matrix of R phase; X500.



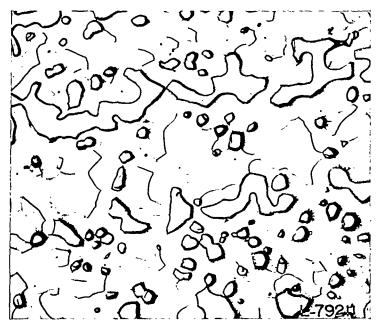


FIGURE 24.—Alloy 513 containing 19.88 percent chromium, 49.78 percent cobalt, and 30.34 percent molybdenum. Etched and stained according to procedure 3; phase contrast shown in three-phase alpha-sigma-R alloy; alpha is unstained (white), sigma is stained (darkest), and R is lightly stained; X500.

particles were stained but not so clearly delineated as unstained alpha particles. The contrast achieved by procedure 3 is further illustrated in figure 24, where larger amounts of alpha and sigma coexist in a matrix of the R phase. Data from a typical X-ray diffraction pattern of the R phase are presented in table XIII.

Impurity phases.—Three main impurity phases were observed in the microstructures of alloys investigated in this work. Metallic oxide inclusions (mostly chromium oxide) were present in the alloys in varying amounts. The chromium-rich epsilon alloys showed the highest number of oxide inclusions, while alloys rich in nickel and molybdenum showed the least. Metallic oxide inclusions are easily recognized in as-polished and unetched microstructures. They are generally unattacked by etchants. Chromium-oxide particles are visible in figure 13 which is an epsilon alloy etched to bring out the Widmanstätten precipitate of sigma.

Another impurity phase appeared in some alloys which were melted in zirconia or stabilized zirconia crucibles. The amount of this impurity phase was observed to be especially high in an alloy which had been slightly overheated during melting in a stabilized zirconia crucible. The specimen had been forged and homogenized at 1,200° C for 48 hours. The microstructure showed small amounts of sigma second phase associated with a dark etching phase in a network outlining the grains of alpha, suggesting a eutectic origin. This structure is illustrated in figure 25. This alloy was analyzed by quantitative spectrographic analysis and was found to contain more than 1.00 percent zirconium. It was concluded that the impurity phase resulted from the reaction between the molybdenum-containing liquid metal and the crucible.

Minute amounts of a bright yellow impurity phase were found in all alloys which were melted in zirconia or stabilized

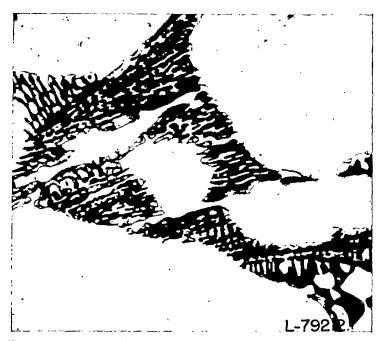


FIGURE 25.—Alloy 376 containing 38.76 percent chromium, 31.2 percent cobalt, 27.54 percent nickel, and 2.5 percent molybdonum. Etched lightly according to procedure 1; dark otching zirconium impurity phase associated with small second-phase particles of sigma in matrix of alpha phase; X2,000.

zirconia crucibles. It is believed that this impurity, too, resulted from zirconium pickup by the alloy. Spectrographic analysis of an alloy melted in an Alundum crucible revealed no aluminum pickup. Microscopic observation did not show any impurity connected with aluminum in any alloy melted in an Alundum crucible. All alloys in the latter part of this work were melted in Alundum crucibles.

PHASE DIAGRAMS

The various phase diagrams determined in the present work are described in the following paragraphs.

Cobalt-nickel-molybdenum ternary system at 1,200° C,-The 1,200° C isothermal section of the cobalt-nickelmolybdenum ternary system, as drawn from alloy data listed in table III, is presented in figure 1. For convenience, the same diagram with the alloy compositions indicated is shown in figure 2. Within the composition ranges investigated, only solid solutions of the phases known from the binary systems were found; no ternary phases occur. About two-thirds of the diagram is covered by the alpha phase field and the two-phase alpha-plus-mu field. The mu phase field penetrates deep into the ternary isothermal section, roughly parallel to the cobalt-nickel side. Limited solid solutions of delta coexist with the mu and alpha phases in two narrow two-phase fields. Alpha, delta, and mu coexist in a three-phase field pointing toward the nickel corner of the diagram.

The face-centered cubic solid solutions based on the cobaltnickel alpha phase extend to 36 percent molybdenum on the nickel-molybdenum side and to 22.5 percent molybdenum on the cobalt-molybdenum side of the diagram. This is in good agreement with the published nickel-molybdenum and cobalt-molybdenum binary systems. The solubility limit of the alpha phase in the ternary isothermal section is slightly concave, running from the cobalt-molybdenum side ECHNICAL LIBRARY

to the corner of the three-phase alpha-delta-mu field (point 10, fig. 1), and almost a straight line from the corner of the three-phase field to the nickel-molybdenum binary diagram. The corner of the three-phase field on the alpha boundary (point 10, fig. 1) is placed at 10 percent cobalt, 35 percent molybdenum, and 55 percent nickel. This point was located by combined microscopic and X-ray data. Alloy 627 contained very small amounts of both the delta and mu phases. In order to check the microscopic findings, the lattice parameters of saturated alpha alloys along the boundary were plotted as a function of cobalt content. The corner of the three-phase field is usually indicated by a sudden change in the slope of the parameter curve. This plot is presented in figure 26 from data listed in table XIV. It is evident from figure 26 that the general effect of cobalt going into solid solution in the saturated nickel-molybdenum alpha phase is to contract the lattice. Unfortunately, however, there were not enough points on the parameter curve to locate the cusp accurately. The point at which the parameter curve suddenly changes slope was definitely located by determining the parameter of the alpha participating in the three-phase field. Since the composition of the alpha is constant anywhere in the three-phase field, the lattice parameter is also constant. The composition corresponding to this point on the parameter curve (point 10, fig. 26) gives the location of the three-phase-field corner. Within the limits of experimental accuracy, this point lies between 9.50 and 10.50 percent cobalt. This result is in excellent agreement with the microscopic findings. Tests were made on the reproducibility of parameter measurements on the same alloy. The lattice parameter of an alpha alloy which gave diffraction rings that were particularly difficult to read (intensity maximums due to preferred orientation) was determined

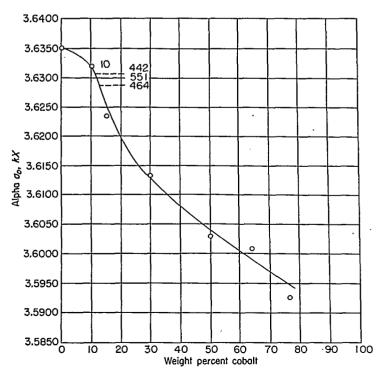


FIGURE 26,—Variation of lattice parameter at 1,200° O of alpha boundary alloys in cobalt-nickel-molybdenum ternary system plotted as function of cobalt content.

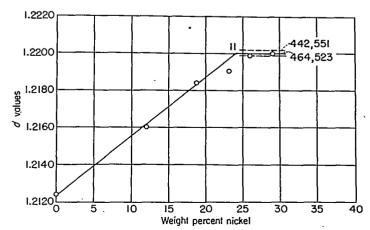
from five different films, each one taken after replacing the specimen on the camera. The maximum variation in these five measurements was 0.001 kX unit. A similar check on an alloy which produced sharp, smooth diffraction rings gave a maximum variation in five measurements of only 0.0003 kX unit.

In alloy 407 a large discrepancy was found between the intended melted analysis and the reported chemical analysis. Both analyses are reported in table III. The reported chemical analysis, however, moves the location of the alloy almost parallel to the alpha boundary so that the course of the boundary is not changed. The intended analysis is plotted in figure 2.

Solid solutions based on the mu phase extend to at least 24 percent nickel (point 11, fig. 1) in the cobalt-nickel-molybdenum 1,200° C isothermal ternary section. This was confirmed by X-ray investigation. As nickel goes into solid solution, the lattice of the mu phase expands gradually, becoming constant in the two-phase delta-plus-mu field and in the three-phase field. The d values for a high-angle X-ray line in a series of mu alloys were plotted as a function of nickel content, as shown in figure 27. The solubility limit is indicated at 24 percent nickel (point 11, fig. 27). The d values for the same line in patterns of mu for alloys located in the three-phase field were determined as a further check. As seen from the data given in table XV, the agreement was

The alpha and mu phases coexist in a large two-phase field extending from the cobalt-molybdenum side of the diagram to the corners of the three-phase field on the alpha and mu phase boundaries. The corner of the three-phase field on the mu phase boundary (point 11, fig. 1) is placed at 17 percent cobalt, 24 percent nickel, and 59 percent molyb-

The delta phase extends to only 6.5 percent cobalt in the isothermal section and coexists with alpha in a two-phase field which extends from the nickel-molybdenum side of the diagram to the corners of the three-phase field on the alpha and delta phase boundaries. The corner of the three-phase field on the delta phase boundary (point 12, fig. 1) was found to be at 6.5 percent cobalt, 33.5 percent nickel, and 60 percent molybdenum.



TOURE 27.—Variation at 1,200° C of d values of twenty-eighth X-ray diffraction line of mu phase in cobalt-nickel-molybdenum ternary system plotted as innotion of nickel content,

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The composition range of the three-phase alpha-delta-mu field is outlined by the three corners (points 10, 11, and 12, fig. 1) given above. The obtuse angle of this triangular field is at the delta corner.

Chromium-cobalt-molybdenum ternary system at 1,200° C.—Figure 3 is the 1,200° C isothermal section of the chromium-cobalt-molybdenum ternary system, drawn in accordance with the alloy data listed in table IV. The same diagram is presented in figure 4 with alloy compositions indicated. In addition to solid solutions of the phases known from the binary systems, a new ternary phase, not known in any of the binary systems, was discovered. This new ternary phase was designated as the R phase. Solid solutions of the face-centered cubic alpha phase surround the cobalt corner of the diagram. The chromium-cobalt sigma phase extends approximately halfway across the isothermal section in a field roughly parallel to the chromium-molybdenum side of the diagram, and solid solutions based on the cobalt-molybdenum mu phase occur in a small field, also approximately parallel to the chromium-molybdenum side. The R phase field is located between the ends of the sigma and mu phase fields. The extension of the mu and R phase fields in the direction parallel to the cobalt-molybdenum side of the diagram was not investigated in detail. Alpha coexists with the sigma and mu phases in two wide two-phase fields and with the R phase in a long, narrow two-phase field. The R phase coexists with the sigma and mu phases in two narrow two-phase fields. The alpha, sigma, and R phases coexist in a three-phase field between the alpha-sigma and alpha-R two-phase fields. Alpha, R, and mu coexist in a three-phase field between the two-phase fields of alpha and R and of alpha and mu.

The solubility of chromium in cobalt at 1,200° C was determined by Manly and Beck (reference 1) at 34 percent. In the present work the solubility of molybdenum in cobalt was found to be 22.5 percent. This value is approximately 1.00 percent lower than that indicated by the cobaltmolybdenum diagram reported by Sykes and Graff (reference The difference is of the order of magnitude of experimental error. The alpha phase boundary in the 1,200° C isothermal ternary section is a convex curve from the chromium-cobalt binary to the corner of the three-phase alphasigma-R field (point 13, fig. 3) and almost a straight line from the cobalt-molybdenum binary to the corner of the alpha-sigma-R three-phase field. There is a slight cusp on the alpha boundary at the corner of the three-phase alpha-Rmu field (point 16, fig. 3). The alpha-sigma-R three-phasefield corner (point 13, fig. 3) is placed at 21.0 percent chromium, 66 percent cobalt, and 13 percent molybdenum, while the corner of the alpha-R-mu three-phase field (point 16. fig. 3) is at 16 percent chromium, 69 percent cobalt, and 15 percent molybdenum. In figure 28, the lattice parameters of saturated alpha alloys along the alpha phase boundary are plotted as a function of chromium content. Data for this plot are given in table XVI. The three-phase-field corners on the alpha phase boundary are clearly indicated by sharp breaks in the parameter curve. The breaks occur at approximately 14.5 and 21.0 percent chromium (points 13

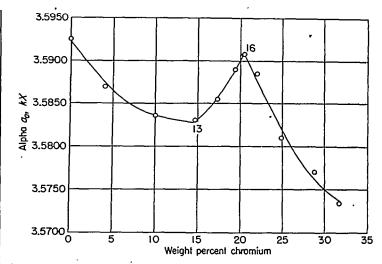


FIGURE 28.—Variation of lattice parameter at 1,200° C of alpha boundary alloys in chromium-cobalt-molybdenum ternary system plotted as function of chromium content.

and 16, fig. 28), agreeing well with the microscopic work. (The reason for the sudden decrease and increase in parameters at the corners is, explained under "Discussion.")

The sigma phase field is a narrow band, from 40 to 45 percent cobalt, which penetrates to a maximum of 31 percent molybdenum in the 1,200° C isothermal ternary section. The corner of the three-phase alpha-sigma-R field on the sigma phase boundary (point 14, fig. 3) is at 25 percent chromium, 46.5 percent cobalt, and 28.5 percent molybdenum. Evidence was found in the microstructure of alloy 531 that another three-phase-field corner occurs on the sigma phase boundary at approximately 27 percent chromium, 42 percent cobalt, and 31 percent molybdenum. This may be a corner of a three-phase sigma-epsilon-R field. It was observed from X-ray diffraction patterns of the sigma phase that the lattice expands as the amount of molybdenum in solid solution increases. No quantitative plot of d values against composition was made to check the solubility limit, however, because the end of the sigma phase field was easily located by microscopic means.

The two-phase alpha-plus-sigma field extends from the chromium-cobalt side of the diagram to the corners of the three-phase alpha-sigma-R field on the alpha and sigma phase boundaries.

The third corner of the alpha-sigma-R three-phase field (point 15, fig. 3) is on the boundary of the R phase at 18 percent chromium, 44 percent cobalt, and 38 percent molybdenum. The obtuse angle in this triangular field is at the sigma corner.

The solubility limits of the R phase in the direction parallel to the chromium-molybdenum side of the diagram were located at approximately 14.5 and 19.5 percent chromium. The alpha-R-mu three-phase-field corner on the R boundary (point 17, fig. 3) is placed at 13.5 percent chromium, 44 percent cobalt, and 42.5 percent molybdenum. The other corner of this very narrow three-phase field (point 18, fig. 3) is on the boundary of the mu phase at 9.5 percent chromium, 42.5 percent cobalt, and 48 percent molybdenum. The obtuse angle in this triangular field is at the corner on the R phase boundary.

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The alpha-plus-R two-phase field is located between the three-phase fields of alpha, sigma, and R and of alpha, R, and mu.

The mu phase takes a maximum of approximately 11 percent chromium into solid solution and coexists with alpha in a large two-phase field extending from the cobalt-molybdenum binary to the corners of the three-phase alpha-R-mu field on the alpha and mu phase boundaries.

Chromium-nickel-molybdenum ternary system at 1,200° C.-The 1,200° C isothermal section of the chromium-nickelmolybdenum ternary system was drawn from data given in table V and is presented in figure 5. The same diagram with the alloy compositions indicated is shown in figure 6. Besides the phases known from the binary systems two new ternary phases were found to occur in the composition ranges investigated. One of these ternary phases has the familiar sigma structure and was, therefore, designated sigma. The crystal structure of the other new ternary phase, designated as the P phase, is unknown. About three-quarters of the area of the diagram, within the range of compositions investigated, is covered by solid solutions of the alpha phase around the nickel corner and by two-phase fields and threephase fields in which alpha coexists with the epsilon, sigma, P, and delta phases. The large two-phase fields of alpha and sigma and of alpha and P are separated by a very narrow three-phase alpha-sigma-P field. A narrow three-phase alpha-P-delta field lies between the alpha-P and alpha-delta two-phase fields. The alpha and epsilon phases coexist in a two-phase field along the chromium-nickel side of the diagram. The three-phase alpha-sigma-epsilon field, which separates the alpha-epsilon and alpha-sigma two-phase fields, is relatively large in comparison with the other threephase fields. The ternary sigma phase coexists with epsilon and P in 2 two-phase fields. Delta and P coexist in a small two-phase field.

At 1,200° C solid solutions of face-centered cubic nickel in the chromium-nickel binary system extend to 57.5 percent chromium and in the nickel-molybdenum binary system, to 36 percent molybdenum. The alpha phase boundary in the ternary isothermal section has a sharp peak at the alpha corner of the three-phase alpha-epsilon-sigma field (point 19, fig. 5). This point was located by microscopic means at 43 percent chromium, 53.5 percent nickel, and 3.5 percent molybdenum. Except for a slight cusp at the alpha corner of the other three-phase fields (points 22 and 25. fig. 5), the alpha boundary is fairly straight from the nickelmolybdenum binary to the alpha corner of the three-phase alpha-epsilon-sigma field. From data listed in table XVII, the lattice parameters of saturated alpha alloys along the alpha boundary were plotted in figure 29 as a function of chromium content. The alpha-epsilon-sigma three-phasefield corner on the alpha boundary (point 19, fig. 5) is very clearly indicated at about 43 percent chromium by the drastic break in the curve (point 19, fig. 29). The curve is almost vertical beyond this point because the chromium content of saturated alpha coexisting with the epsilon phase varies between only 43 and 42.5 percent. The break in the parameter curve at 23 percent chromium (point 22, fig. 29),

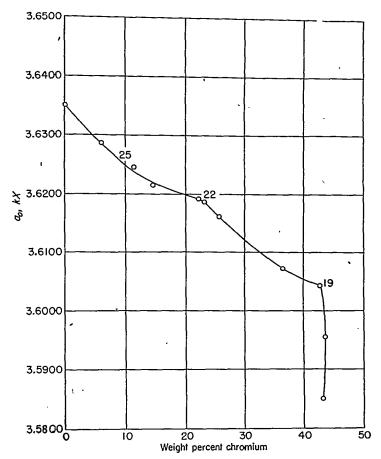


FIGURE 29.—Variation of lattice parameter at 1,200° O of alpha boundary alloys in chromiumnickel-molybdenum ternary system plotted as function of chromium content.

though not so drastic, is also in good agreement with the location of the three-phase alpha-sigma-P field corner (point 22, fig. 5) from microscopic findings. The alpha corner of the three-phase alpha-P-delta field (point 25, fig. 5) is not manifested by a pronounced cusp and is almost imperceptible. This point was located at 6 percent chromium, 61.5 percent nickel, and 32.5 percent molybdenum by carefully determining the boundaries of the three-phase alpha-P-delta field. Extrapolated segments of the parameter curve indicate a break at approximately 7.5 percent chromium (point 25, fig. 29), in fair agreement with the above observations.

The epsilon boundary was determined only along the two-phase alpha-epsilon field. This boundary extends from the chromium-nickel side of the diagram to the epsilon corner of the three-phase alpha-epsilon-sigma field (point 20, fig. 5). As shown in figure 5, alpha, epsilon, and sigma coexist in a three-phase field whose boundaries are as follows: The alpha corner (point 19, fig. 5) at 43 percent chromium, 53.5 percent nickel, and 3.5 percent molybdenum; the sigma corner (point 21, fig. 5) at 49 percent chromium, 28 percent nickel, and 23 percent molybdenum; and the epsilon corner (point 20, fig. 5) at 60 percent chromium, 29.5 percent nickel, and 10.5 percent molybdenum.

The sigma phase field is approximately parallel to the chromium-molybdenum side of the diagram, comprising a range of about 23 to 49 percent chromium. As molybdenum replaces chromium in the sigma structure, the lattice expands.

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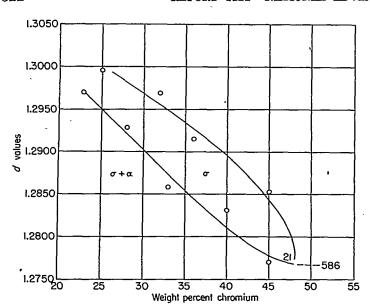


Figure 30.—Variation at 1,200° C of d values of twenty-third X-ray diffraction line of sigma phase in chromium-nickel-molybdenum ternary system plotted as function of chromium content.

This is clearly illustrated in figure 30, which was plotted from the data given in table XVIII. The variation of one high-angle d value for a series of saturated sigma alloys along both sides of the sigma field is shown as a function of chromium content. The two curves meet at approximately 48 percent chromium (point 21, fig. 30), corresponding closely to the sigma corner of the three-phase alpha-epsilon-sigma field (point 21, fig. 5).

Solid solutions of the new ternary P phase exist between 8 and 19 percent chromium. The two-phase fields of P and sigma and of P and delta are very narrow, each one extending over a range of only about 4 percent chromium.

The corners of the three-phase alpha-sigma-P field are located at the following points: The alpha corner (point 22, fig. 5) at 23 percent chromium, 57.5 percent nickel, and 19.5 percent molybdenum; the sigma corner (point 23, fig. 5) at 22 percent chromium, 31 percent nickel, and 47 percent molybdenum; and the P corner (point 24, fig. 5) at 19 percent chromium, 32.5 percent nickel, and 48.5 percent molybdenum.

At 1,200° C the nickel-molybdenum delta phase dissolves only about 4 percent chromium. This phase coexists with alpha in a long, narrow, almost rectangular two-phase field along the nickel-molybdenum binary system.

The boundaries of the extremely narrow three-phase alpha-P-delta field are located by the following points: The alpha corner (point 25, fig. 5), as described above; the P corner (point 26, fig. 5) at 8 percent chromium, 34.5 percent nickel, and 57.5 percent molybdenum; and the delta corner (point 27, fig. 5) at 4 percent chromium, 37.5 percent nickel, and 58.5 percent molybdenum.

Some discrepancies were noted in a few alloys of chromium, nickel, and molybdenum near the three-phase alpha-epsilon-sigma field. The microstructure of alloys 475, 569, and 597 showed only two phases, alpha and sigma, although, according to the intended compositions of these alloys, they should contain three phases. Chemical analysis of these alloys

moved 569 and 597 into the two-phase alpha-sigma field, thus removing the discrepancy for these two alloys. Alloy 475, however, still remained in the three-phase alpha-epsilon-sigma field. In drawing the phase boundary between the two-phase alpha-sigma and the three-phase alpha-epsilon-sigma fields, alloy 475 was neglected. The microstructure of alloy 640 showed small amounts of the epsilon phase. The chemical analysis of this alloy, however, would place it in the sigma phase field. Both the melted and chemical analyses are given in table V, but the intended melted analysis is plotted in figure 6. Alloys 598 and 600 contained more sigma than would be expected from the phase diagram. This is probably a result of the difficulty in obtaining equilibrium in chromium-rich alloys.

Small amounts of a phase not explainable from the phase diagram were observed in alloys 622 and 447. The identity of this phase is not known. It may have resulted from nonequilibrium or segregation. Small particles of this unknown phase are shown in figure 31, where second-phase particles of alpha in a sigma matrix are also seen.

Alpha boundaries in constant-molybdenum sections of chromium-cobalt-nickel-molybdenum quaternary system at 1,200° C.—Figure 7 is a 1,200° C isothermal diagram in which the alpha phase boundaries for the 2.5-, 5-, 10-, and 20-percent-molybdenum sections through the chromium-cobalt-nickel-molybdenum quaternary system are plotted. Figure 8 is the same diagram with the alloy compositions from table VI indicated.

At constant temperature a quaternary phase diagram is represented by a tetrahedron, each corner point of which corresponds to 100 percent of one component. The four faces of the tetrahedron, then, are isothermal sections of four ternary systems, and the six edges are isothermal binary sections. In the chromium-cobalt-nickel-molybdenum qua-



FIGURE 31.—Alloy 447 containing 40 percent chromium, 30 percent nickel, and 30 percent molybdenum. Etched and stained according to procedure 2; small particles of phase not identifiable from figure 6 plus unstained alpha in matrix of sigma phase; X750.

ternary system at 1,200° C sections of constant molybdenum content are triangular sections through the tetrahedron parallel to the chromium-nickel-cobalt face. As the amount of molybdenum increases, the size of the equilateral triangle becomes smaller. Because of this change in size, these sections cannot be superimposed upon each other for the purpose of showing, in a two-dimensional diagram, the limits of a phase in the quaternary system. In order to facilitate the diagrammatic presentation of results and to allow direct comparison of the effect of increasing molybdenum content, on the alpha boundary, the following method was used: Each section of constant molybdenum content was projected onto the chromium-cobalt-nickel ternary isothermal section by using the molybdenum corner of the tetrahedron as the center of projection. This projection may be accomplished arithmetically by increasing proportionately the percentages of chromium, cobalt, and nickel in the quaternary composition to add up to 100 percent and then plotting quaternary compositions as if they were ternary chromium-cobaltnickel compositions. The correction factor for each section is the inverted fraction of the total amount of chromium, cobalt, and nickel in the quaternary composition. For example, in a quaternary alloy containing 20 percent molybdenum, 10 percent chromium, 10 percent cobalt, and 60 percent nickel, the chromium, cobalt, and nickel represent eight-tenths of the total composition. Multiplying the quaternary percentages of chromium, cobalt, and nickel by the inverted fraction, that is, 10/8, gives the projection of this quaternary point on the chromium-cobalt-nickel ternary diagram. While the molybdenum content of alloys used to fix the alpha boundaries was actually never exactly 2.5, 5, 10, or 20 percent, the corresponding boundaries were corrected by factors of 10/9.75, 10/9.5, 10/9, and 10/8, respectively. The results are shown in figure 7, using this method of plotting. An alternative method was used in figure 32 where the actual solubility of chromium in the alpha phase at the various constant molybdenum levels is plotted as a function of actual cobalt content. The data for these curves were interpolated from figure 7 and are tabulated in table XIX. The alpha phase boundary in the 1,200° C isothermal section of the chromium-cobalt-nickel ternary system was determined by Manly and Beck (reference 1) and is included for comparison.

As seen from figures 7 and 32, increasing the molybdenum content decreases the solubility of chromium in the alpha phase, thereby decreasing the extent of the alpha field at 1,200° C. At the chromium-nickel side of the diagram the solubility of chromium in alpha first increases slightly and then rapidly decreases beyond about 5 percent molybdenum.

No attempt was made to identify the phases which coexist with the alpha phase in the quaternary system, but some general statements can be made from observations of the chromium-cobalt-molybdenum and chromium-nickel-molybdenum ternary systems at 1,200° C. On the chromium-cobalt side of the diagram the sigma phase coexists with alpha from 0 to approximately 12.5 percent molybdenum. Between 12.5 and approximately 16 percent molybdenum the

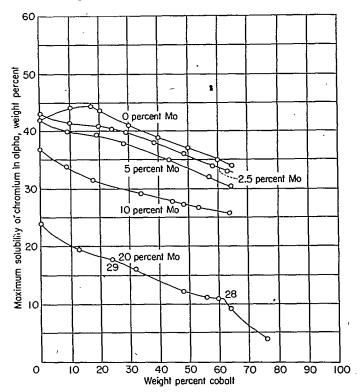


FIGURE 32—Maximum solubility at 1,200° O of chromium in alpha phase of chromiumcobalt-nickel-molybdenum alloys plotted as function of actual cobalt content for constant molybdenum contents of 2.5, 5, 10, and 20 percent.

ternary R phase coexists with the alpha phase at the chromium-cobalt side of the diagram. Above 16 percent molybdenum the mu phase coexists with alpha. On the chromium-nickel side of the diagram the alpha phase coexists with epsilon from 0 to approximately 3 percent molybdenum and with the ternary sigma phase between 3 and about 19 percent molybdenum. The ternary P phase coexists with alpha on the chromium-nickel side between 19 and 33 percent molybdenum. The delta and quaternary alpha phases coexist over very limited composition ranges, above 33 percent molybdenum. It is not known whether the chromiumcobalt-molybdenum and chromium-nickel-molybdenum sigma phases form an uninterrupted series of solid solutions through the quaternary system at 1,200° C, although there is some basis for expecting it, as stated under "Discussion."

In the 2.5-, 5-, and 10-percent-molybdenum alpha boundaries no sharp breaks were found from the metallographic data, and X-ray parameter plots are not available to check this. However, in figure 32, there is some indication of a cusp on the 2.5- and 5-percent alpha boundaries at approximately 20 percent actual cobalt content. Evidence of two corners on the 20-percent-molybdenum alpha phase boundary was found, one being at approximately 61 percent actual cobalt content (point 28, fig. 32) and the other, at approximately 24 percent actual cobalt content (point 29, fig. 32). The lattice parameters of saturated alpha alloys along this boundary were plotted as a function of actual cobalt content in figure 33. The data for this plot are given in table XX. Two distinct breaks occur in the curve of parameter against composition at approximately 24 and 62 percent actual



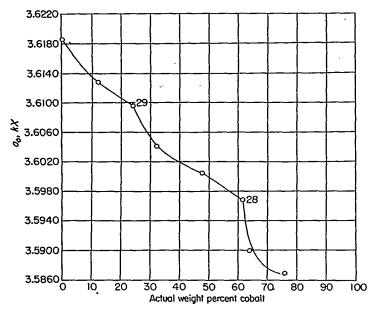


FIGURE 33.—Variation of lattice parameter at 1,200° O of alpha boundary alloys in 20-percentmolybdenum section of chromium-cobalt-nickel-molybdenum quaternary system plotted as a function of actual cobalt content.

cobalt content (points 28 and 29, fig. 33). This is in good agreement with the microscopic results.

DISCUSSION

In view of the fact that the face-centered cubic (alpha) solid solutions form the matrix of almost all practically useful high-temperature alloys, the extent of the alpha phase field in the chromium-cobalt-nickel-molybdenum quaternary system and in the four adjoining ternary systems at 1,200° C is of great interest. The alpha phase field in the 1,200° C isothermal section of the chromium-cobalt-nickel ternary system was shown previously to be very broad (reference 1). In the cobalt-nickel-molybdenum ternary system, also, the alpha phase field is quite large. As the cobalt content increases, the solubility of molybdenum in the alpha phase decreases from 36 percent in the nickel-molybdenum binary system at 1,200° C to 22.5 percent molybdenum in the cobaltmolybdenum system. Both the delta and mu phases, which coexist with alpha in the cobalt-nickel-molybdenum ternary system at 1,200° C, are very hard, although their presence in alpha alloys does not appear to have nearly so drastic an effect on toughness as that of the sigma phase.

Solid solutions of the alpha phase surround the cobalt corner of the chromium-cobalt-molybdenum ternary isothermal section and the nickel corner of the chromium-nickel-molybdenum ternary isothermal section. In both of these systems the extent of the alpha phase field is small in comparison with the chromium-cobalt-nickel and the cobalt-nickel-molybdenum alpha fields. It is interesting to note that in the chromium-nickel-molybdenum isothermal section the sigma phase coexists with alpha above 3.5 percent molybdenum. The fact that the brittle sigma phase may precipitate out of supersaturated alpha containing more than 3.5 percent molybdenum is of great practical importance, since considerable amounts of the sigma phase may seriously impair the forging characteristics of alpha alloys.

In the chromium-cobalt-nickel-molybdenum quaternary system the extent of the alpha phase field at 1,200° C becomes smaller as the molybdenum content increases. In quaternary alloys above 36 percent molybdenum alpha probably does not occur in a single phase field, although it coexists with other phases up to approximately 61 percent molybdenum.

Some interesting features were observed in the variation of lattice parameter of alpha with composition. (reference 19) has shown that the general effect of increasing cobalt content in nickel-cobalt binary alloys is to increase the lattice parameter of the alpha phase. Figure 26 shows that the lattice parameter of saturated nickel-molybdenum alpha decreases with increasing cobalt content. Also, from figure 33, along the alpha boundary in the 20-percent constant-molybdenum quaternary section, the lattice parameter again decreases with increasing cobalt content. denum going into binary solid solution increases the lattice parameter of both nickel and cobalt. Although nickel itself has a smaller a_0 than cobalt, the lattice parameter of saturated nickel-molybdenum alpha is larger than that of saturated cobalt-molybdenum alpha. Apparently, chromium has the same general effect as molybdenum. The peculiar variation of the lattice parameter along the alpha boundary in the 1,200° C isothermal section of the chromium-cobalt-molybdenum ternary system (fig. 28) may be interpreted as shown in figure 34, which is a schematic sketch of the ternary section with isoparameter lines drawn in the alpha phase field. The decrease of lattice parameter beyond the corner of the three-phase alpha-sigma-R field results from the intersection of lower and lower isoparameter lines with the alpha phase boundary. At the alpha-R-mu three-phase-field corner, the lattice parameter reaches a minimum value, and beyond this point the alpha boundary again intersects successively higher isoparameter curves until the cobalt-molybdenum side of the diagram is reached.

The accuracy of the location of the alpha phase boundaries is estimated to about ±1 percent of any component. Chemical analysis of all definitive boundary alloys gave generally good correlation with intended compositions. Any large discrepancies were usually found to be errors in chemical analysis, although, in some instances referred to in the description of results, the alloy compositions appeared to be in fact different from the intended compositions.

The occurrence of the brittle intermetallic sigma phase in alloy systems involving the transition elements is interesting from both the fundamental and practical viewpoints. The presence of sigma, even in small amounts, in high-temperature alloys is undesirable because of the brittleness which it imparts to alloys. The composition ranges over which sigma exists are, therefore, important. In the cobalt-nickel-molybdenum ternary system at 1,200° C the sigma phase does not occur. However, solid solutions of the chromium-cobalt sigma phase penetrate deep into the 1,200° C isothermal section of the chromium-cobalt-molybdenum ternary system, and in this system sigma coexists with alpha below 13 percent molybdenum (fig. 3). In the present investigation a ternary sigma phase was found in the 1,200°

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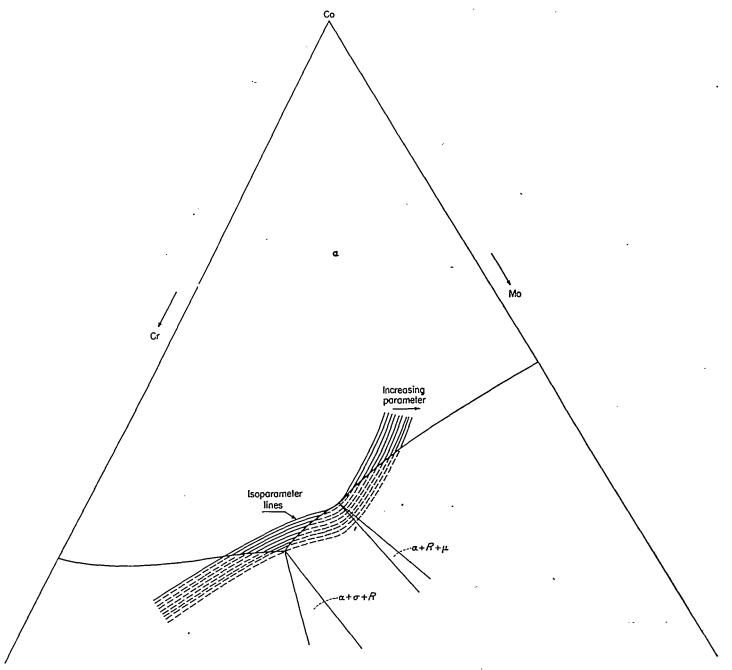


FIGURE 34.—Schematic sketch of alpha-phase-field boundary at 1,200° C in chromium-cobalt-molybdenum ternary system with hypothetical isoparameter lines shown.

C isothermal section of the chromium-nickel-molybdenum ternary system. The sigma phase in this system was also found independently by Putman, Grant, and Bloom (reference 20). In a discussion of their paper, Beck (reference 20) presented a tentative diagram for the chromium-nickel-molybdenum ternary system at 1,200° C. This diagram was refined in the present investigation and is presented in figure 5. At 1,200° C the sigma phase coexists with alpha in chromium-nickel-molybdenum alloys containing from 3.5 to 19 percent molybdenum.

The sigma phases in the chromium-cobalt-molybdenum and chromium-nickel-molybdenum ternary systems may form a continuous series of solid solutions in the chromium-cobalt-nickel-molybdenum quaternary system at 1,200° C. If such quaternary sigma solid solutions do occur, the sigma phase might very likely coexist with alpha in the 1,200° C isothermal quaternary section over wide ranges of the alpha

phase boundary in alloys containing 3.5 to 13 percent molybdenum. Some indication that the sigma phases do form an uninterrupted series of quaternary solid solutions is found in the 10-percent constant-molybdenum section. The alpha boundary in this section has no pronounced break suggestive of a three-phase-field corner, and sigma does coexist with alpha at both ends of the phase boundary.

The shape and location of the sigma phase field in the chromium-cobalt-molybdenum and chromium-nickel-molybdenum isothermal sections give further support to the previous observation (reference 15) that atoms of transition elements having the same crystal structure can substitute for each other in the formation of the sigma phase. In the chromium-cobalt-molybdenum isothermal section (fig. 3) the sigma phase field extends in a direction parallel to the chromium-molybdenum side of the diagram, and approximately half of the chromium is replaced by molybdenum.

ranges over which the sigma phases occur in terms of electron vacancy concentration calculated from this formula. Almost all of the binary and ternary sigma phase fields were found to fall within a rather narrow range of electron vacancy concentration. The favorable range of concentration seems to be from 3.15 to $3.65N_{\rm g}$. It appears that the composition ranges of other intermetallic phases occurring in alloy systems of transition elements can also be defined in terms of electron vacancy concentration, although some overlapping may occur.

Again in the chromium-nickel-molybdenum ternary isothermal section (fig. 5) the ternary sigma phase occurs in a long, narrow field parallel to the chromium-molybdenum side of the diagram. In these two systems body-centered cubic transition elements are substituting for each other. In the chromium-cobalt-nickel ternary system at 1,200° C the sigma phase field is parallel to the cobalt-nickel side of the diagram, indicating that nickel is replacing cobalt (both face-centered cubic) while the chromium content remains essentially unchanged (references 1 and 15).

As the molybdenum content of the sigma phase increases, the lattice expands in both the chromium-cobalt-molybdenum and the chromium-nickel-molybdenum systems. It is interesting that an X-ray diffraction pattern of a chromium-cobalt-molybdenum sigma alloy saturated with molybdenum is almost identical to a pattern of chromium-nickel-molybdenum sigma of the lowest molybdenum content.

The existence of a ternary sigma phase in the chromiumnickel-molybdenum ternary system is rather unexpected, as none of the adjoining binaries are known to have a sigma phase. From the results of the investigation of the 1,200° C isothermal section of the chromium-cobalt-nickel ternary system, Beck and Manly (reference 15) suggested that the nickel-chromium system, which is not reported to include any intermediate phase, might contain a sigma phase at some lower temperature, and Duwez and Baen (reference 16) note that, according to the criteria postulated by them, the nickel-chromium system would be expected to have a sigma phase. The ternary sigma phase found in the chromiumnickel-molybdenum system may have some connection with the suspected nickel-chromium binary sigma phase. tempts were made to confirm this by annealing for long periods of time an alloy of 38 percent nickel and 62 percent chromium at temperatures below 600° C. These experiments were, however, not successful. This does not rule out the possibility of the existence of sigma in this system at a temperature so low that the diffusion rates are prohibitively

From the experimental results of this and other investigations of alloy systems in which the sigma phase occurs, a criterion for the formation of the sigma phase was developed in terms of electron vacancy concentration in the 3d subband. Details of this development are given in reference 21. Briefly, the procedure is to calculate the electron vacancy concentration N_{\bullet} in any alloy from the 3d sub-band electron vacancies in each component of the alloy, and from the atomic percent concentration of the components. Electron vacancy numbers for chromium, cobalt, and nickel were given by Pauling (reference 22; see also reference 23). Molybdenum was assumed to have the same number of vacancies in the 4d sub-band as chromium has in the 3d sub-band, on the basis that their electronic structure is similar in the outermost shells. The formula for calculating N_{\bullet} is given as

 N_{\bullet} =4.66(Cr+Mo)+3.66(Mn)+2.66(Fe)+1.71(Co)+0.61(Ni)

It was found possible to define fairly well the composition

There are some interesting features connected with the solid solutions designated mu in the present investigation. For example, the mu phase, commonly referred to as epsilon in the cobalt-molybdenum binary system, is isomorphous with the corresponding intermediate phase in the iron-molybdenum, cobalt-tungsten, and iron-tungsten binary systems (reference 11). Köster and Tonn (reference 24) reported that the mu phases in the iron-molvbdenum and cobaltmolybdenum binary systems form a continuous series of solid solutions across the 1,300° C isothermal section of the iron-molybdenum-cobalt ternary system. In the ironmolybdenum-cobalt system the mu phase field extends in a direction approximately parallel to the iron-cobalt side of the diagram, so that the face-centered cubic elements iron and cobalt substitute for each other while the molybdenum content remains unchanged. As shown in the present work, solid solutions of the mu phase extend more than halfway across the 1,200° C isothermal section of the cobalt-nickelmolybdenum ternary system (fig. 1). Here, again, the face-centered cubic elements cobalt and nickel replace each other, while the molybdenum content remains essentially unchanged. The body-centered cubic elements chromium and molybdenum seem to replace each other in forming the mu phase in the 1,200° C isothermal section of the chromiumcobalt-molybdenum ternary system (fig. 3), with the cobalt content remaining constant. In agreement with these observations one would expect that solid solutions of the mu phase in ternary systems of iron, cobalt, molybdenum, and tungsten would also extend in such a manner that atoms of elements having the same crystal structure could substitute for each other. The intermediate nickel-molybdenum delta phase forms only limited solid solutions in the cobalt-nickelmolybdenum and chromium-nickel-molybdenum isothermal sections (figs. 1 and 5).

In addition to the ternary sigma phase, another new ternary phase P was discovered in the 1,200° C isothermal section of the chromium-nickel-molybdenum ternary system. The P phase field is located between the ends of the sigma and delta phase fields (fig. 5). In physical characteristics and microstructure the P and sigma phases are very much alike, but the X-ray diffraction patterns of the two phases are quite different. The differentiation between P and sigma provides a good example of the need to supplement microscopic work with X-ray diffraction to identify the phases. In alloys consisting wholly of P or sigma it was impossible to identify the phase present by any of the microscopic techniques used in this investigation, even though it was possible to differentiate microscopically between sigma and P when they occurred side by side in the same alloy.

The 1,200° C isothermal section of the chromium-cobaltmolybdenum ternary system was also found to contain a ternary phase, located between the ends of the sigma and mu phase fields (fig. 3). This phase R has a distinctive X-ray diffraction pattern (table XIII) and it is easily differentiated microscopically from the sigma or mu phases when these phases occur in the same alloy. However, as in the case of chromium-nickel-molvbdenum ternary sigma and P phases, chromium-cobalt-molybdenum alloys consisting wholly of the R or sigma phases could not be differentiated microscopically (except possibly by microhardness). Final identification was made in all cases by X-ray diffraction.

CONCLUSIONS

A survey at 1,200° C of portions of the chromium-cobaltnickel-molybdenum quaternary system and of the component cobalt-nickel-molybdenum, chromium-cobalt-molybdenum, and chromium-nickel-molybdenum ternary systems indicated the following conclusions:

- 1. A portion of the 1,200° C isothermal section of the cobalt-nickel-molybdenum ternary system was investigated, using 47 vacuum-melted alloys with molybdenum contents up to a maximum of 62 percent. The system features an extensive range of face-centered cubic (alpha) solid solutions based on the cobalt-nickel binary system, solid solutions based on the nickel-molybdenum binary delta phase, and solid solutions based on the cobalt-molybdenum binary mu phase. The narrow delta and mu phase fields penetrate into the ternary system to 6.5 percent cobalt and 24 percent cobalt, respectively, and coexist in a narrow two-phase deltaplus-mu field. The alpha phase coexists with the delta and mu phases in two wide two-phase fields and an alpha-deltamu three-phase field.
- 2. A portion of the 1,200° C isothermal section of the chromium-cobalt-molybdenum ternary system was determined, using 85 vacuum-melted alloys with molybdenum contents up to a maximum of 53 percent and cobalt contents of 35 percent and more. The phases present in this composition range were found to be the face-centered cubic (alpha) solid solutions around the cobalt corner, solid solutions based on the chromium-cobalt binary sigma phase, solid solutions based on the cobalt-molybdenum binary mu phase, and a new ternary phase R, of fairly small composition range, which does not appear in any of the binary systems. The sigma phase was found to extend in an elongated field from the chromium-cobalt binary into the ternary system along a line of approximately constant cobalt content of 45 percent, taking molybdenum into solution up to a maximum of 31 percent, so that up to about half of the chromium is replaced by molybdenum. The R phase, comprising a range of chromium contents from about 14.5 to 19.5 percent, is located between the ends of the sigma phase field and of the mu phase field, and it coexists with the sigma and mu phases in 2 two-phase fields. The cobalt-molybdenum binary mu phasé extends into the ternary system up to approximately 11 percent chromium. The alpha face-centered cubic solid solutions coexist with the sigma, R, and mu phases in three rather wide two-phase fields and two narrow three-phase fields of alpha, sigma, and R and of alpha, R, and mu.
- 3. The 1,200° C isothermal section of the chromiumnickel-molybdenum ternary system was investigated in the composition range of 0 to 59 percent molybdenum and 18 to 100 percent nickel, using 119 vacuum-melted alloys. The following phases were located: The face-centered cubic (alpha) solid solutions around the nickel corner, the bodycentered cubic (epsilon) solid solutions based on chromium, solid solutions based on the nickel-molybdenum binary delta phase, the ternary sigma solid solutions which, at 1,200° C, are not connected with any of the binary systems, and another ternary phase P, which has not been encountered in any of the binary systems. The ternary sigma phase is located in a long, narrow field between about 21 and 49 percent chromium and approximately 23 to 30 percent molybdenum, which extends approximately parallel to the chromium-molybdenum side of the ternary diagram, as found also in the chromiumcobalt-molybdenum ternary system. Here, too, the shape and location of the sigma field indicate that chromium and molybdenum can substitute for each other in forming the sigma phase. Successive pairs of the epsilon, sigma, P, and delta phases coexist in 3 two-phase fields. The alpha solid solution coexists with the epsilon, sigma, P, and delta phases in 4 two-phase fields and 3 three-phase fields of alpha, epsilon, and sigma; alpha, sigma, and P; and alpha, P, and delta. The two-phase alpha-plus-sigma field covers an extensive area, starting at molybdenum contents as low as 3.5 percent.
- 4. The alpha solid-solution phase boundary in the chromium-cobalt-nickel-molybdenum quaternary system at 1,200° C was determined for constant molybdenum contents of 2.5, 5, 10, and 20 percent. The over-all effect of molybdenum additions to the chromium-cobalt-nickel ternary system at 1,200° C is to decrease the extent of the facecentered cubic (alpha) solid solutions, that is, to shift the alpha phase boundary toward lower chromium contents. At 1,200° C the alpha phase boundary in the 2.5-percentmolybdenum section is essentially the same as that in the chromium-cobalt-nickel ternary system, except near the chromium-nickel side, where it is moved toward higher chromium contents. The phases which coexist with the alpha phase in the 2.5-percent-molybdenum section are sigma and epsilon. In the 5-percent constant-molybdenum section the alpha-phase-boundary shift becomes more evident, although the magnitude of the shifting is still relatively small. The sigma phase is seen to coexist with the alpha solid solutions near both the chromium-cobalt and the chromium-nickel sides of the diagram. This is due to the presence of the ternary sigma phase in the chromium-nickelmolybdenum ternary system at 1,200° C. The alpha phase also coexists with epsilon and sigma in a three-phase field near the chromium-nickel side of the diagram. The shift of the alpha phase boundary toward lower chromium contents is more pronounced in the 10-percent-molybdenum section of the isothermal quaternary system. Again the sigma phase is seen to coexist with the alpha solid solutions at both the chromium-cobalt and the chromium-nickel ends of the alpha phase boundary. The alpha phase also coexists with epsilon and sigma in a three-phase field near the chromium-nickel side of the diagram. The alpha phase bound-

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ary in the 20-percent-molybdenum section is shifted to 4 percent chromium on the chromium-cobalt side of the diagram and to 30 percent chromium on the chromium-nickel side. The mu phase coexists with the alpha solid solutions near the chromium-cobalt side of the quaternary section, whereas the ternary P phase coexists with the alpha phase at the chromium-nickel end of the alpha phase boundary.

5. The results of this investigation give further support to the conclusion that atoms of both face-centered and body-centered cubic transition elements are required to form the sigma phase and that elements having the same crystal structure can substitute for each other. It appears that the same criterion may hold for ternary solid solutions of the cobalt-molybdenum intermediate mu phase, which is isomorphous with the corresponding intermediate phases in the iron-molybdenum, cobalt-tungsten, and iron-tungsten binary systems. The composition ranges over which the sigma phases exist can be described fairly well in terms of electron vacancy concentration in the 3d sub-band. This suggests a criterion for predicting whether or not the sigma phase may occur within any given composition range in alloy systems involving the transition elements.

University of Notre Dame, Notre Dame, Ind., January 31, 1951.

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TABLE I LOT ANALYSES BY WEIGHT PERCENT

Element or compound	Cobalt rondelles	Chromium	Nickel	Molybdenum
C CaO Co		0.01	0.6 to 0.8	0.003 max.
Cr Cu Fe	.02 .12	Bal. Trace .06 .045	.01 .01	.005 max.
MgO Mn Mo N:	.04	.010		Bal.
NI Ot Pb SiOt	.009	.51 .001 .012	BaL .001	.003 approx,

TABLE II
CRUCIBLES USED FOR MELTING ALLOYS

Zirconia	Stabilized zirconia	Alundum
273 311 to 314 320 322 402 to 405 414 to 419	323 330 to 332 354 360 to 362 366 376 to 383	272 280 288 289 206 to 298 321 370 to 372 375 384 to 401 407 to 413 420 to 715

SURVEY OF PORTIONS OF THE CHROMIUM-COBALT-NICKEL-MOLYBDENUM QUATERNARY SYSTEM AT 1,200° C 329

TABLE III DATA FOR THE PHASE DIAGRAM OF THE COBALT-NICKEL-MOLYBDENUM SYSTEM AT 1,200° C

	Amelmal	a (malaht r		Phase	s from fl	gure 2		Ph	ases (per	cent) found from—	
Alloy	Allaiysi	s (weight p	ereent)		(percent)		Mi	crostruc	ture	X-ray	Annea ing time (hr)
	Co	Ni	Mo	Alpha	Delta	Mu	Alpha	Delta	Mu	Ariay	(11.)
'				<u> </u>	Alpl	a bound	ary alloy	78 *			·
399	77.08	-12	22.92	98		2	95		5	Alpha	48
400 401	30	65 40	35 30	100 98		2	100 100		Trace	Alpha	48 48 56
407	20 17.4	50 50	30 32. 6	100			100			Alpba	l
408 426	49.63 32	24.95 42	25. 43 26	99 100		1	100 100		Trace	Alpha	65 48
427		68	26 32	100			100			Alpha	48
432 440	79 50	28	2I 22	100 100			100 100			Alpha	48
441	20	57	23 23.64	100			100			Alpha	48
461 462	49.89 20	26. 47 54	23.64 26	100 100			100 100			Alpha	48
486		62.92	26 37. 08	97		3	95	5		Alpha	65
498 540	20 65	53 12	27	100 100			100 100			Alpha	48
541	10	58	27 23 32 25	100			100			Alpha	48 48 48 48 48 48 48 48 48 48 48 48 48
552 553	754 10	11 56	25 34	98 100		2	98 100		4	Alpha	48
b 620	30. 24	40.84	28.92	100			100			Alpha	48
627 679	10.2 15	53.72 52	36.08 33	98 100	Trace	Trace	96 100	1	Trace	Alpha	48 48
0,8	1 10			100				<u> </u>	111000	Anpha	10
	·				Alp	ha-plus-	mu alloy	8 0		,	
421	55	-11	45	30		70	25		75	Alpha plus mu	91
442 443	15 25	35 25	50 50	40 30		60 70	50 25		50 75	Alpha plus muAlpha plus mu	95 95
444	35	15	50	20		80	25		75	Alpha plus mu	92
530 546	18.28 14	24.12 46	57.60 40	75		99	5 80		95	MuAlpha plus mu	98
547	18	42	40	70		25 30	75		20 25	Alpha plus mu	98
548	22 22	38	40 50	70		30 65	75 5		25 95	Alpha plus mu	98
554 715	12	28 48	40	35 80		20	75		25	Alpha plus mu	95
		· 		/	·	Mual	loys °	·	· ' · · · · · · · · · · · · · · · · · · 	· · · · · · · · · · · · · · · · · · ·	·
b 550	22. 74 23	18.77	58. 49			100			100	Mu	95
596 629	20	16 20	61 60			100 100			100 100	Mu	95
	<u> </u>	'	<u></u>	·	Alph	a-plus-de	lta alloy:	3 •		/	•
414		49	51	40	60		50	50		Alpha plus delta	91 91 91
465 520	5 4	45 38 35 36	50 58	45 10	55 90		50 15	50 85		Delta	9.
521	7	35	58 58 60	10	90	Trace	12	85	3	Delta	9
677	4	38	60	1	99	<u> </u>	Trace	100		Delta	9.
			··	,	De	lta-plus-	mu alloy	8 •		,	
▶ 595 ▶ 628	7.05 7.22	30. 78 32. 65	62.17 60.13		95 98	5 2	₁	95 95	5 4	Delta Delta	9. 9.
	1	l	l	1	<u> </u>	1	plus-mu	<u> </u>	<u> </u>	1	<u> </u>
	10	10	50	T	1	30	40		30	Alpha plus delta plus mu	9.
101	10	40	1 50 20	b 10	35 60	30	15	30 70	15	Delta plus mu	9.
464 522	10	32	20								
464 522 523 537	10 13 16	29 26	50 58 58 58	10 5	25 10	65 85	10	iŏ	80 95	Delta plus mu	I 9.

<sup>All forged prior to annealing.
Ohemical composition from analysis. Composition given for other alloys is the intended melted analysis.
Not forged prior to annealing.</sup>



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TABLE IV DATA FOR THE PHASE DIAGRAM OF THE CHROMIUM-COBALT-MOLYBDENUM SYSTEM AT 1,200° C

	(m)	Analysis	nt)	P	hases fro	om figure	4 -				found fr percent)	om	Anneal-
Alloy	(#6	eight perce	nt)		(pe	псень)			Micros	tructure		X-ray	ing time (hr)
	Cr	Co	Mo	Alpha	Sigma	R	Mu	Alpha	Sigma	R	Mu	A-lay	
						Alpha b	oundary	alloys •					
272 366 378 378 437 430 431 433 443 443 443 443 443 443 443 443	33.15 29.45 30.31 10 10 20 20 10 3 28.83 4 21.61 22.5 14.88 9.88 25.61 21.42 14.7	64. 35 65. 55 65. 96 77. 08 77 70 70 70 68 74 77 64. 8 76. 4 64. 5 69. 78 72. 99 64. 5 68. 61 68. 65	2.5 5.3.73 22.92 18 14 10 21 12 16 20 6.87 20 8.99 13,64 17,13 10,65	90 100 100 98 95 100 100 100 100 100 100 100 100 100 10	10		7 Trace	85 100 100 95 90 100 100 100 100 100 90 100 100 90 100 95 100 98	15		75 10	Alpha	48 48 48 48 48 48 48 48 48 48 48 48 48 4
	<u>',</u>		•	·		Alpha-p	lus-sigmo	alloys •					
273 288 314 322 330 330 384 5398 470 474 512 538 547 547 558 555 668 682	31. 28 38. 02 36. 1 36. 8 34. 16 42. 3 31. 7 29 32. 22 27 28. 5 38 28 41 23. 3 33. 75 7. 2	60. 72 59, 48 58, 9 55, 2 63, 41 51, 7 62 47, 57 53 51, 5 48 46 45, 6	8 2. 5 5 8 2. 43 6 5. 21 9 20. 21 20 14 26 14 20. 62 21. 27 47. 2	75 65 62 50 87 35 87 85 15 40 20 5 5 5 5 8	25 35 38 50 13 65 13 15 85 55 60 80 95 45 92			65 60 60 80 90 40 90 80 15 80 50 50 50 50	35 40 40 50 10 60 10 20 85 50 75 95 90 90	Trace		Alpha Alpha plus sigma Alpha plus sigma Alpha plus sigma Alpha Alpha Sigma plus alpha Alpha Alpha Alpha Sigma Alpha plus sigma	96 96 96 105 66 96 96 145 145 96 96 146 150
	·	·· ······		·	,	Alpha-	plus-R a	lloys •			··, . · ·	······································	
533 558 560 592	19.36 16 19.81 16 18	65. 29 52 57. 9 60 44	15. 35 32 22. 29 24 38	90 40 55 60 2		10 60 45 40 98		90 50 50 60 2		10 50 50 40 98		Alpha plus R	76 96 96 96 150
						Alpha-p	lus-mu al	loys •				· ·	
534 535 544 573	11, 6 8 7. 86 12. 7	54, 27 56 43, 05 61, 31	34. 13 36 49. 09 25. 99	45 50 5 65			55 50 95 35	50 50 5 75			50 50 95 25	Alpha plus mu Alpha plus mu Mu Alpha plus mu	96 96 96 96

<sup>All forced prior to annealing.
Chemical composition from analysis.
Not forced prior to annealing.
Not forced prior to annealing.</sup>

SURVEY OF PORTIONS OF THE CHROMIUM-COBALT-NICKEL-MOLYBDENUM QUATERNARY SYSTEM AT 1,200° C 331 TABLE IV—Concluded

DATA FOR THE PHASE DIAGRAM OF THE CHROMIUM-COBALT-MOLYBDENUM SYSTEM AT 1,200° C

	(we	Analysis	nt)	P	hases fro	m figure	4			Phases (r	found froercent)	om—	Anneal;
Alloy					· · · · · · · · · · · · · · · · · · ·				Micros	tructure		X-ray	ing time (hr)
	Cr	Co	Mo	Alpha	Sigma	R	Mu	Alpha	Sigma	R	Mu	A-lay	
					Alph	a-plus-si	gma-plus	-R alloys	3 4				
6 513 556 605 633 649	19.88 24 18.5 22.5 24.5	49.78 50 45.5 46.5 47	30.34 26 36 31 · 28.5	20 18 8 5 5	5 80 2 70 90	75 2 90 25 5		20 20 9 10 5	10 80 1 70 90	70 Trace 90 20 5		R plus alpha	96 96 96 96 150
	<u></u>		' <u></u>	·	Aır	ha-plus-	R-plus-n	ıu alloys	•		<u> </u>	<u>, </u>	·
\$ 559 \$ 585 680 \$ 681	13.67 13.76 11.5 9.82	53. 12 60. 99 44 43. 03	33. 21 25. 25 44. 5 47. 15	40 70 2 4		59 10 43 Trace	1 20 55 96	40 75 2 2		60 10 48 Trace	Trace 15 50 98	R plus alpha Alpha plus mu Mu plus R Mu	96 96 96 96
	<u>'</u> -		'	·		Sign	na alloys		·				L.—
392 393 423 472 473 485 500 530 531 543 590 594 624 625	52.6 56.4 34 39.97 33.99 41.3 32.37 28.37 28.27.1 30 28.5	41. 4 37. 6 36 40. 56 43 42. 94 38. 56 42. 4 40. 69 46 42. 4 42. 4 45. 5	6 6 30 19.47 20.14 26 30.94 26 10 30.5 28 27.5		100 100 100 100 100 100 100 100 100 100			Trace	100 80 75 100 100 100 95 100 4 95 100 100 100 100	Trace		Sigma	150 150 150 150 150 150 150 150 150 150
						Sigma-	plus-R al	loys •	. — —	- 1	<u> </u>		
650	24. 42 19. 79 24 19	45.82 41.95 43 44	29. 76 38. 26 34 37		85 10 60 15	15 90 40 85		 	80 10 50 25	20 90 50 75		Sigma R Sigma plus R R	150 96 96 96
	·					F	alloys •						
6 514 6 591	15. 71 13. 78	41. 69 43. 89	42.60 42.33			100 100				100 100		R	96 96
						R-plu	s-mu allo	ys •					
515 668	12 16	41 40	47 44			40 98	60 2			50 95	50 5	Mu plus R	96 96
						м	u alloys	•	r —				·
516 545 574 5630 631	6 11 8.51 9.4 10	41 38 40.37 42.8 42	53 51 51,12 47,8 48	 2			100 99 100 98 98	2			100 96 100 98 98	Mu	96 96 96 96 96

Chemical composition from analysis. Composition given for other alloys is the intended melted analysis.
 Not forged prior to annealing.
 Also two second phases.



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TABLE VDATA FOR THE PHASE DIAGRAM OF THE CHROMIUM-NICKEL-MOLYBDENUM SYSTEM AT 1,200° C

	Analys	is (weight	percent)	P	hases fro	m figure	6 (perce	nt)			F	hases (p	ercent) fo	ound from—	Anneal
Alloy		· ·	· ·		т	 -	- -			М	icrostruc	ture		X-ray	ing time (hr)
	Cr	NI	Mo	Alpha	Epsilon	Sigma	P	Delta	Alpha	Epsilor	Sigma	P	Delta	,	
								Alpha	alloys						
360 375 382 400 427 433 434 437 - 437 - 438 454 486 688	42, 51 39, 9 40, 56 	55. 08 55. 1 54. 92 65 68 64 58 54. 28 57. 31 62. 5 62. 92 61. 75	2. 41 5 4. 52 35 32 26 16 9, 73 17. 21 27. 5 37. 08 33. 25	100 100 100 100 100 100 100 100 100 100		Trace		Trace	100 100 100 100 100 100 100 100 100 100		Trace		Trace	Alpha	48 48 48 48 48 48 48 48 48 48 48
	<u></u> -	<u> </u>	<u>'</u>		<u>. </u>	' <u>.</u>	Alp	ha-plus-e	osilon al	loys •	<u> </u>	<u>'</u>	1	<u>'</u>	<u>'</u>
298 311 387 404 449 562 563 614	56, 33 43, 37 53, 86 70, 5 60 60 57, 5 43, 5	41, 17 54, 17 40, 28 23, 6 30 35 35 53	2.5 2.46 5.86 6 10 5 7.5 3.5	55 95 50 5 5 35 30 98	45 5 50 95 95 65 70 2				50 95 50 10 10 40 30 95	50 5 50 90 90 60 70 5				Alpha plus epsilon Alpha Alpha plus epsilon Epsilon Epsilon Epsilon Epsilon plus alpha Epsilon plus alpha Alpha	96 48 96 96 96 96 96 96
				-			Alı	ha-plus-a	igma all	o ys •					
389 410 411 418 435 446 447 451 452 476 477 478 480 482 488 481 491 569 570 608 617 608 617 641 663 684	42.75 42.76 45.25 45.25 328 329 46.35 41.88 283 27.5 45.5 45.5 45.5 22.25 5 5	52. 25 54. 35 55 56 55 56 56 57 57 67 57 67 57 57 58 58 58 58 58 58 58 58 58 58 58 58 58 58 58 5	5 20 12 20 12 20 12 20 12 20 12 20 12 20 12 20 12 20 20 12 20 20 20 20 20 20 20 20 20 20 20 20 20	95 85 85 85 85 85 85 85 85 85 85 85 85 85		5 15 17 5 2 2 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5			95 90 80 25 97 52 5 60 60 50 50 50 50 40 10 50 40 25 57 57 5 70 5 70 5 70 5 70 5 70 5 70		5 100 207 5 5 75 5 40 40 50 50 50 75 80 80 80 80 80 80 80 80 80 80 80 80 80			Alpha. Alpha. Alpha. Alpha. Sigma plus alpha Alpha. Alpha plus sigma Sigma plus alpha Sigma plus sigma Alpha plus sigma Alpha plus sigma Alpha plus sigma Sigma plus alpha Sigma plus alpha Sigma plus alpha Sigma Alpha plus alpha Sigma Sigma Sigma Alpha plus sigma Sigma Sigma Alpha plus sigma Sigma Sigma Alpha plus sigma Sigma	48 56 56 56 56 56 56 56 56 56 56 56 56 56
,							Al	pha-plus-	P alloys						
409 415 460 460 468 467 468 469 510 579 612 638 664 689	10 20 22. 9 14. 28 20 10 10 10 22. 09 10 15. 57 11. 28 21. 25 6. 41	60 40 56, 45 59 50 55 45 57, 33 33, 72 33, 72 35 48, 23 53, 48	30 40 20, 65 26, 72 30 35 45 20, 58 55, 21 56, 5 29, 26 30, 52 40, 11	95 35 90 95 75 80 35 95 5 3 95 65 65			5 65 10 5 25 25 20 65 5 97 97 7 35		93 30 95 98 80 75 50 95 3 5 6 70			7 70 5 2 20 20 25 50 5 97 95 95 30		Alpha P plus alpha Alpha Alpha Alpha Alpha plus P Alpha plus P P plus alpha Alpha PP P P Alpha plus P P Alpha plus P P Alpha P P Alpha P P Alpha P P Alpha P	48 96 48 96 96 96 96 48 96 96 48 96 96 48
				·				lpha-plu	s-delta s	lloys •					
414 691 692	4.5 4.5	49 54. 5 46	51 41 49. 5	40 70 40				60 30 60	50 75 50				50 25 50	Alpha plus delta	95 96 90

<sup>All forged prior to annealing.
Chemical composition from analysis.
Not forged prior to annealing.</sup>

SURVEY OF PORTIONS OF THE CHROMIUM-COBALT-NICKEL-MOLYBDENUM QUATERNARY SYSTEM AT 1,200° C 333

TABLE V-Concluded DATA FOR THE PHASE DIAGRAM OF THE CHROMIUM-NICKEL-MOLYBDENUM SYSTEM AT 1,200° C

	Analysi	s (weight p	oreant)	101	hases fro	m flaum	g (nomeon	+\			P	hases (pe	ercent) fo	ound from—	Anneal-
Alloy	Allaiyad	- (weight)				m neme	o (percen			Mi	crostruct	ure		¥	ing time
į	Cr	Ni	Мо	Alpha	Ep s flon	Sigma	P	Delta	Alpha	Epsilon	Sigma	P	Delta	X-ray	(hr)
							Alpha-	plus-epsi	lon-plus-	igma all	0y 3 ¢				
320 448 448 450 476 564 565 586 586 588 588 600 622 655 672	43. 7 48. 66 49. 82 47. 5 52. 5 55. 5 51. 6 55. 85 48. 5 50. 43. 5	51. 3 31. 25 37. 19 40 35 34. 54 30 29 28. 73 35. 1 45. 4 28 52. 25	5 20. 09 12. 99 13. 10. 5 12. 96 15 20 18. 67 9. 05 6. 1 22 4. 25 11. 5	90 15 30 45 35 20 10 5 23 85 Trace 94 2	Trace 5 30 5 50 40 50 20 38 75 34 10 1 93	10 80 40 50 15 40 40 75 80 2 1 90 5			90 10 35 50 25 30 20 5 5 50 50 50 75 75 75 75	1 10 25 35 50 20 20 20 30 10 Trace 80	9 80 40 50 20 35 30 75 75 20 20 85 5			Alpha Sigma Sigma plus epsilon Sigma plus alpha Epsilon plus sigma Epsilon plus sigma Epsilon plus sigma Sigma Sigma Sigma Epsilon plus alpha plus sigma Alpha plus epsilon plus sigma Alpha Epsilon plus sigma	150 150 150 150 150 150
							Alp	ha-plu s -s	igma-plu	s-P alloy	78 4				
568 • 613 642 669	20 19.3 21.25 22	35 32. 5 32 49	45 48. 2 46. 75 29	30 5 5 70		30 5 95 15	40 90 Trace 15		30 10 5 75		30 15 95 10	40 75 Trace 15		P plus sigma P Sigma Alpha	96 96 96 96
 	,		 .	,			Alpi	ha-plus-l	-plus-de	lta alloy:					·
635 670 690	7 7.1 5.5	45 35. 8 54	48 57.1 -40.5	38 5 70		-2	60 70 10	2 25 20	50 8 70			50 87 10	Trace 5 20	P plus alpha Alpha plus delta	.1961
								Eps	llon alloy	g e					
397 599 618 676	76. 2 65 61 65	17. 8 22 27 25. 75	6 13 12 9. 25		100 100 98 100	2			Trace	100 100 100 100	Trace			Epsilon Epsilo	150 150 150 150
					<u> </u>	·	Epsi	lon-plus	-sigma al	loys •	·		·		
419 567 587 640 643	61 52.5 51.99 47.6 49 59	19 25 27. 19 27. 2 27. 5 28	20 22. 5 20. 82 25. 2 23. 5 13		35 25 2 2	65 75 98 				65 30 30 5 5	35 70 70 95 40			Sigma plus epsilon Sigma Sigma Sigma Epsilon plus sigma	.i 150 i
				·	·	·		Sign	na alloys	•		•			
416 481 493 508 509 511 527 577 578 602 603 604 685	34 37 47 32 25, 06 38 31 31, 5 30, 5 25 36 45 22, 5	26 28 23 25 26, 12 22 24, 5 26, 5 27, 5 24 25 30	40 35 30 45 48. 82 40 44 43 47. 5 40 30 47. 5			100 100 28 100 100 100 100 100 100					100 100 100 90 90 95 90 100 100 100 100 100			Sigma	96 96 96 96 96
								Sigma	plus-P a	lloys *					
"528 686 492	22 23. 5 20	28 27. 5 30	50 49 50			50 80 10	50 20 90				50 90 4	50 10 96		Sigma plus P	96 96 96
								Pal	loys •						
580	15	30	55				100					100		P	96
	,			,				Delta	alloys •				1	<u> </u>	
529 561 626 671	5 2.81 4 4	36 36. 67 36. 5 37. 25	59 60. 52 59. 5 58. 75	1			30 2 	70 100 98 99	Trace			40 Trace	60 100 100 100	Delta plus P	96 96 96 96

Chemical composition from analysis. Composition given for other alloys is the intended melted analysis.
 Not forged prior to annealing.
 Also 10 percent of a second phase.
 Also two second phases.



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TABLE VI DATA FOR THE PHASE DIAGRAM OF THE CHROMIUM-COBALT-NICKEL-MOLYBDENUM SYSTEM AT 1,200° C

	An	nalysis (we	ight percen	ıt)	Phases	from (percent	figure 8		- , 		md from—	Anneal-
Alloy	Cr	Co	Ni	Мо	Alpha	Sigma	Epsilon	<u> </u>	zostruct Sigma	Epsilon	X-ray	time (hr)
-	1	<u>I</u>	<u> </u>	2.5-perc	ent-moly	bdenum	quaterna	ry alloys	'	J	<u> </u>	<u> </u>
280 288	42.9 38.02	16.58 . 59.48	38.02	2.5 2.5	65	35		+ 99 60	40		Alpha plus	48 96
289 296 297 311 312 313 323 330 331 332 354 360 361 362 372 376	35. 1 38. 02 44. 35 43. 37 40. 95 34. 16 36. 84 42. 51 42. 51 41. 94 39. 98 40. 46 38. 76 43. 39	63. 4 44. 85 15. 6 31. 2 9. 75 31. 2 63. 41 45. 13 9. 75 31. 90 	14.63 37.05 54.17 25.35 42.9 27.3 15.61 43.87 28.08 46.12 33.16 32.66 27.54 44.36	25546 2255432 2252222 245843 2255 2255 2255 2255	85 	13	5	90 95 95 95 98 99 98 100 100 100 100 100 100 100 10	10	5	sigma Alpha	\$6 48 48 48 48 48 48 48 48 48 48 48 48 48
	<u> </u>		<u></u>	5-perce	nt-molyl	odenum	quaterna	ry alloys•	<u> </u>			\
314 320 321 386 375 378 389 380 381 382 383 390 428 428 428 429 431 435 437 507 517 518 623 623 623	36. 1 43. 7 29. 49 30. 30 30. 30 30 30 30 30 30 30 30 30 30 30 30 30 3	58. 9 19- 65. 55 65. 96 42. 49 10. 8 9. 34 10 17. 14 63. 09 42. 45 27. 83 28. 5 70 48. 6 18 48. 6 18 33. 90 48. 25 9. 25	51. 3 32. 3 55. 1 18. 72 37. 84 45. 78 54. 92 46. 56 53. 89 17. 16 29. 62 29. 45 53. 63 54. 26 37. 8 14. 3 26. 87 40. 52 53. 88 54. 88 56 56 56 56 56 56 56 56 56 56 56 56 56	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	62 90 100 100 100 100 100 95 100 87 100 100 98 100 98 100 100 100 100 100 100 100 100	38 10	Trace	90 90 100 100 100 100 100 95 98 100 90 90 98 100 90 98 100 90 98 100 90 98 100 90 90 90 90 90 90 90 90 90	40 9 	1	Alpha plus sigma Alpha	96 75 48 48 48 48 48 48 48 48 48 48 48 48 48
,1				20-percen	t-molybo	lenum q	uaternar;	y alloys •				
]				Alpha	Р	Mu	Alpha	P	Mu		
456 • 457 • 458 • 469 • 469 • 488 • 489 • 490 • 501 • 503 • 504 • 505 • 652 • 652	3 22.9 16 11. 2 22.09 4 16 20. 8 24 9.0 14.8 19.0 12.0 18.4 11.2 4	77 24 48 32 12.8 04 48 32 24 12.8 24 12.8 24 12.8 61.6 47.7	56. 45 40 20. 8 57. 33 16 27. 2 43. 2 6. 4 17. 2 28. 8 35. 2 45. 6 47. 2 37. 6 47. 2 37. 6 19. 3	20 20, 65 20 20, 58 20, 58 20 20 20 20 20 20 20 20 20 20 20 20 20	100 90 100 100 95 100 	5	Trace	100 95 100 100 100 85 100 88 88 88 88 88 88 88 88 88 88 88 88 8	5	Trace	Alpha	48 48 48 48 48 48 48 48 48 48 48 48 48 4

<sup>All forged prior to annealing.
Remaining percentage is unidentified second phase.
Chemical composition from analysis. Composition given for other alloys is the intended melted analysis.
Also trace of unidentified second phase.</sup>

TABLE VII '

TYPICAL X-RAY DIFFRACTION PATTERN OF FACE-CENTERED CUBIC ALPHA PHASE

Line	Estimated intensity	8	đ	Radiation Or K	hkl
1 2 3 4 5 6 7 8	Medium Strong Very weak Medium Very weak Weak Very weak	29.86 33.17 35.21 39.30 54.84 63.85 64.01 73.53	2.089 2.089 1.804 1.805 1.272 1.273 1.273 1.085	Beta	111 111 200 200 220 220 220 220 311

TABLE VIII

TYPICAL X-RAY DIFFRACTION PATTERN OF BODY-CENTERED CUBIC EPSILON PHASE

Line	Estimated intensity	θ	đ	Radiation Cr K	hkl
1 2 3 4 5 6 7 8	Medium strong. Strong. Strong. Weak. Weak. Very weak Medium weak. Strong. Medium strong.	30.69 34.13 46.43 52.75 52.87 62.64 77.42 77.89	2.039 2.037 1.435 1.435 1.435 1.171 1.171	BetaAlphaBetaAlphaBetaAlphaBetaAlphaBetaAlphaAl	110 200 200 200 200 211 211 211

TABLE IX

TYPICAL X-RAY DIFFRACTION PATTERNS OF CHROMIUM-NICKEL-MOLYBDENUM AND CHROMIUMCOBALT-MOLYBDENUM SIGMA PHASES

				, 					 -
Line	Estimated intensity	θ.	đ	Radiation Or K	Line	Estimated intensity	θ	ď	Radiation Cr K
	Or-Ni-Mo sigma phase determined from alloy 587								
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	Medium Medium weak Medium strong Strong Strong Strong Medium Very weak Very very weak Very very weak Medium weak	25.65 14 0.25 75.65 17.82 25.15 17.56 75.85 11.15 17.56 75.85 11.1	2. 672 2. 318 2. 445 2. 445 2. 337 2. 336 2. 004 2. 173 2. 160 1. 917 2. 003 1. 904 1. 844 1. 844 1. 789 1. 672	Alpha. Beta. Alpha. Alpha. Alpha. Alpha. Beta. Beta. Alpha. Alpha. Beta. Alpha.	2012234256778880132334358578	Very weak Very very weak Weak Medium Medium weak Weak Very very weak Weak Very weak Very weak Very weak Very weak Weak Very weak Weak Very weak	58. 02 58. 14 61. 04 63. 72 64. 77 65. 77 65. 77 65. 77 65. 78 66. 18 67. 03 68. 95 69. 67 74. 68 75. 04	1. 347 1. 347 1. 306 1. 276 1. 278 1. 263 1. 255 1. 255 1. 251 1. 251 1. 243 1. 243 1. 226 1. 218 1. 218 1. 218 1. 218 1. 218	Alphai.
		(Or-Co-Mo	sigma phase o	letermi	ned from alloy 530			
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20	Very weak Very weak Weak Weak Medlum weak Medlum Medlum Weak Medlum strong Medlum Medlum Medlum Strong Strong Strong Strong Medlum Weak Very weak Very weak Very weak	28.31 28.65 29.44 31.38 32.19 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 33.86 34.86 35.86 36 36.86 36 36 36 36 36 36 36 36 36 36 36 36 36	2. 651 2. 314 2. 473 2. 410 2. 382 2. 305 2. 305 2. 160 1. 913 2. 053 2. 000 1. 965 2. 000 1. 965 1. 786 1. 786 1. 787 1. 391	Alpha, Beta. Alpha, Alpha, Alpha, Alpha, Beta. Alpha,	21 22 23 24 25 26 27 28 29 30 31 33 34 35 36 37 38 40	Very weak Very very weak Medlum strong Medlum Medlum weak Medlum strong Medlum weak Weak Weak Weak Weak Weak Weak Weak Very weak Weak Weak Very weak Weak Very weak Very weak Very weak Very weak Very weak Very weak Veak Veak Very weak	58, 28 58, 47 63, 87 64, 027 65, 48 66, 05 66, 05 67, 72 67, 71 67, 93 69, 6 70, 63 75, 43	1. 343 1. 273 1. 273 1. 273 1. 273 1. 282 1. 282 1. 282 1. 282 1. 287 1. 287 1. 239 1. 235 1. 221 1.	Alphai,



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TABLE X TYPICAL X-RAY DIFFRACTION PATTERN OF DELTA PHASE DETERMINED FROM ALLOY 522

Line	Estimated intensity	θ	d	Radiation Or K	Line	Estimated intensity	θ	đ	Radiation Or K
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22	Weak Very weak Weak Very very weak Very weak Weak Medlum weak Strong Weak Very very weak Medlum weak Medlum strong Strong Medlum Me	28. 27 28. 63 29. 90 30. 37 31. 42 31. 43 31. 43 31. 44 31. 44 31	2.679 2.660 2.426 2.384 2.198 2.038 2.203 2.193	Alpha. Alpha. Alpha. Alpha. Beta. Alpha. Beta. Beta. Alpha.	37455788883883885858894444444	Very weak Very very weak Very very weak	38. 91 40. 57. 757. 89 59. 98 63. 94 65. 85 66. 52 66. 52	1.847 1.820 1.728 1.351 1.351 1.351 1.334 1.272 1.263 1.247 1.244 1.244 1.244 1.244 1.237 1.232 1.237 1.263 1.267 1.267 1.268	Alpha.

TABLE XI
TYPICAL X-RAY DIFFRACTION PATTERN OF MU PHASE DETERMINED FROM ALLOY 678

Line	Estimated intensity	θ	đ	Radiation Cr K	Line	Estimated intensity	θ	d	Radiation Or K
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	Medium weak Very weak Medium strong Very weak Very very weak Wedium weak Weak Medium Medium Medium Medium Medium Medium Very very weak Strong Medium weak Medium weak Very very weak Very very weak	29, 26 29, 71 30, 19 30, 57 31, 60 31, 83 32, 52 33, 17 33, 52 33, 52 34, 48	2.608 2.169 2.370 2.330 2.306 2.069 2.045 2.020 2.166 2.125 1.901 2.070 2.045 2.019 1.998 1.952	Alpha. Beta. Alpha. Alpha. Alpha. Beta. Beta. Alpha. Beta. Alpha. Alpha. Alpha. Alpha. Alpha. Alpha. Alpha. Alpha. Alpha.	17 18 19 20 21 22 23 24 25 26 27 28 29 30 31	Weak Very weak Very very weak Very very weak Very very weak Very very weak Weak Very weak Very weak Weak Weak Medlum weak Weak Medlum weak Medlum weak Weak	36. 92 38. 95 39. 76 56. 73 59. 64 59. 80 61. 62 62. 61 70. 26 74. 83 75. 19	1. 903 1. 817 1. 787 1. 366 1. 386 1. 324 1. 301 1. 288 1. 216 1. 216 1. 184 1. 184	Alpha,

TABLE XII
TYPICAL X-RAY DIFFRACTION PATTERN OF P PHASE DETERMINED FROM ALLOY 580

Line	Estimated intensity	θ	đ	Radiation Or K	Line	Estimated intensity	8	đ	Radiation Or K
1 2 3 4 5 6 7 8 9 10 11 12 13 114 15 16 17 18 19 20 21 22 23 24	Very weak Very very weak Very very weak Very very weak Weak Medium weak Medium weak Medium weak Medium weak Medium weak Weak Weak Weak Weak Weak Weak Weak Medium	55.82 55.55.56 56.55.56 56.55.56 56.55.56 56.55.56 56.55.56 56.55	2.650 2.388 2.381 2.392 2.191 2.381 2.192 2.382 2.192 2.040 2.031 2.197	Alpha. Beta. Beta. Beta. Beta. Alpha. Alpha. Alpha. Alpha. Beta. Alpha. Beta. Alpha. Alpha. Beta. Alpha.	25 26 27 28 30 31 32 33 34 35 36 37 38 39 41 42 43 44 45 47 48	Medium weak Weak Weak Very weak Weak Weak Weak Weak Weak Weak Weak W	36.44 36.707 38.02 39.00 60.03	1.985 1.925 1.910 1.807 1.820 1.317 1.307 1.301 1.255 1.265 1.277 1.299 1.239 1.194 1.199 1.189 1.189 1.189	Alpha.

SURVEY OF PORTIONS OF THE CHROMIUM-COBALT-NICKEL-MOLYBDENUM QUATERNARY SYSTEM AT 1,200° C 337

TABLE XIII

TYPICAL X-RAY DIFFRACTION PATTERN OF R PHASE DETERMINED FROM ALLOY 592

Line	Estimated intensity	θ	d	Radiation Cr K	Line	Estimated intensity	θ	đ	Radiation Cr K
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21	Weak Very strong Very strong Very yeak Very weak Very very weak Weak Medium weak Medium weak Medium weak Medium weak Weak Medium weak Weak Medium weak Weak Medium weak Very weak Weak Strong Strong Medium strong Medium strong Medium strong	54. 18. 18. 18. 18. 18. 18. 18. 18. 18. 18	2.659 2.612 2.632 2.633 2.629 2.173 2.197 2.2197 2.203 2.233	Alpha. Alpha. Alpha. Alpha. Beta. Alpha. Beta. Alpha. Beta. Alpha. Beta. Alpha. Beta. Alpha. Beta. Alpha.	23 24 25 27 28 29 31 23 33 34 35 5 37 38 34 41 42	Medium strong Medium Very weak Weak Very weak Medium weak Very weak Weak Weak Weak Medium weak Very weak Medium weak Weak Medium weak Weak Medium weak Medium weak Medium weak Medium weak Weak Medium weak Weak Medium weak Weak Weak Weak Weak Weak Weak Weak W	37. 22 37. 42 38. 24 40. 22 33. 427 44. 81 54. 48 54. 55 68. 38 68. 68 68. 68 68. 68 68. 68	1.966 1.954 1.880 1.881 1.720 1.293 1.293 1.293 1.203	Alpha,

TABLE XIV

DETERMINATION OF ALPHA THREE-PHASE-FIELD CORNER BY X-RAY DIFFRACTION IN COBALT-NICKEL-MOLYBDENUM SYSTEM

[Data for fig. 26]

Alloy	Weight percent cobalt	Extrapolated value of a _o (kX)
399 552 408 401 679 627 486 464 551 442	77	3. 5925 3. 6008 3. 6028 3. 6133 3. 6225 3. 6320 3. 6351 3. 6287 3. 6300 3. 6307

TABLE XVI

DETERMINATION OF ALPHA THREE-PHASE-FIELD CORNERS BY X-RAY DIFFRACTION IN CHROMIUM-COBALT-MOLYBDENUM SYSTEM

[Data for fig. 28]

Alloy	Weight percent chro- mium	Extrapolated value of a. (kX)
399	0	3. 5925
487	4	3. 5870
413	10	3. 5834
665	14. 7	3. 5832
645	17. 42	3. 5835
412	19. 36	3. 5890
606	21. 98	3. 5896
644	24. 9	3. 5810
471	28. 83	3. 5771
398	31. 7	3. 5773

TABLE XV

DETERMINATION OF SOLUBILITY LIMIT IN COBALT-NICKEL-MOLYBDENUM MU PHASE BY X-RAY DIF-FRACTION

[Data for fig. 27]

Alloy	Weight percent nickel	θ	sin θ	đ
421 678 550 536 537 523 442 464 551	0	70. 45 69. 94 69. 67 69. 59 69. 47 69. 46 69. 45 69. 48 69. 45	0. 94235 . 93953 . 93771 . 93724 . 93649 . 93642 . 93637 . 93650 . 93657	1. 2124 1. 2160 1. 2184 1. 2190 1. 2199 1. 2200 1. 2202 1. 2202

TABLE XVII

DETERMINATION OF ALPHA THREE-PHASE-FIELD CORNERS BY X-RAY DIFFRACTION IN CHROMIUM-NICKEL-MOLYBDENUM SYSTEM

[Data for fig. 29]

Alloy	Weight percent chro- mium	Extrapolated value of a. (kX)
486 688 636 460 469 457 438 435 389 614 •89	0 5.5 11.3 14.3 22.1 23 25.5 36.25 42.75 43.5	3. 6351 3. 6276 3. 6245 3. 6213 3. 6189 3. 6188 3. 6162 3. 6073 3. 6045 3. 5856 3. 5856

•From reference 1; a. redetermined in the present investigation.

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TABLE XVIII

VALUES OF d OF CHROMIUM-NICKEL-MOLYBDENUM TERNARY SIGMA PHASE AS FUNCTION OF CHROMIUM CONTENT

[Data for fig. 30]

Alloy	Weight percent chro- mium	d value 1
509 508 641 482 603 483 604 447 491 586	25.06 32.0 22.76 28.0 36.0 35.0 45.0 45.0 51.0	1. 2996 1. 2969 1. 2970 1. 2978 1. 2916 1. 2857 1. 2853 1. 2769 1. 2768

 1 d values determined from twenty-third line of sigma patterns.

TABLE XX

DETERMINATION OF THREE-PHASE-FIELD CORNERS ON [20-PERCENT-MOLYBDENUM QUATERNARY ALPHA PHASE BOUNDARY

[Data for fig. 33]

Alloy	Actual weight percent cobalt	Extrapolated value of a., (kX)
457	0	3. 6186
524	12.2	3. 6128
525	24.0	3. 0097
526	32.0	3. 6042
652	47.6	3. 6004
651	61.6	3. 5969
501	64.0	3. 5900
487	78.0	3. 5870

TABLE XIX

DATA USED FOR PLOTTING ACTUAL SOLUBILITY OF CHROMIUM IN ALPHA PHASE AT VARIOUS CONSTANT MOLYBDENUM CONTENTS AS FUNCTION OF ACTUAL COBALT CONTENT

[Data for fig. 32]

Weight percent molyb- denum	Weight percent cobalt	Maximum weight per- cent chro- miuminalpha solid solution
00000000	0 10 18 20 30 40 50 60	42. 2 44. 3 44. 5 43. 4 40. 8 38. 6 37. 0 35. 0 34. 0
25555555555555555555555555555555555555	0 9.75 19.5 24.3 29.25 39.0 48.75 58.6 63.4	43. 3 41. 4 40. 9 40. 5 39. 9 38. 0 36. 0 34. 0 33. 2
5 5 5 5 5 5 5	0 9.5 19.0 28.5 43.5 57.0 64.5	42. 2 40. 0 39. 4 37. 6 35. 0 32. 0 30. 5
10 .10 10 10 10 10 10	9.0 18.0 34.2 45.0 48.6 54.0 64.4	36. 9 33. 75 31. 5 29. 25 27. 9 27. 0 26. 6 25. 7
88888888888888888888888888888888888888	0 12:8 24:0 32:0 48:0 56:0 61:5 64:0 72:0	24.0 19.2 17.6 15.6 12.0 11.2 10.8 10.5 9.2 5.6 4.0