# An Investigation of the Systems Formed By Chromium, Molybdenum, and Nickel

by David S. Bloom and Nicholas J. Grant

An investigation of the Cr-Mo-Ni ternary system and attendant binaries has been completed. Some changes in the binary diagrams are shown to be necessary. The 1250°C section of the ternary and the liquidus surface have been delineated. A system of invariant reactions existing above 1250°C has been suggested.

**B**ECAUSE chromium, molybdenum, and nickel are important not only as bases for alloying systems but also as major alloying additions for other refractory metals, a study of the phase diagrams is of great interest and importance. In addition there are interesting features of theoretical value, a number of which are of prime consideration in this work. The major aim was to determine the ternary phase diagram of these metals at and above 1250°C, with sufficient attention given to lower temperatures to permit an understanding of the conditions existing at 1250°C and above.

To understand ternary systems it is essential that accurate information concerning the binary systems be available, which in turn presupposes thorough knowledge of the constituent elements. On the basis of this investigation not only were significant inaccuracies indicated in the binary systems but much consideration had to be given to one of the elements, that is, chromium.

The observation has been made that chromium undergoes a crystal transformation at a temperature near its melting point. Much of the experimental data leading to the detection of this transformation

D. S. BLOOM, formerly Research Assistant, Dept. of Metallurgy, M.I.T., is now Research Metallurgist, Naval Ordnance Test Station, China Lake, Calif., and N. J. GRANT, Member AIME, is Associate Professor, Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

Discussion on this paper, TP 3703E, may be sent, 2 copies, to AIME by April 1, 1954. Manuscript, Sept. 18, 1953. New York Meeting, February 1954. and the effects of this hypothesis on the form of the Cr-Ni phase diagram have already been reported<sup>1, 2</sup> and will not be repeated here.

The experimental methods employed in the investigation have also been covered.<sup>1-3</sup> The purity of the molybdenum utilized in this work showed by qualitative spectrographic analysis that chromium, copper, iron, silicon, and tungsten were present in quantities of 0.1 to 0.001 wt pct.

During the course of the investigation more than 100 melts were made, weighing from 150 to 200 grams each. Each of these melts was sectioned for chemical analysis and for specimens for examination in the as-cast and various heat-treated conditions by X-ray and metallographic means.

All X-ray diffraction patterns reproduced here were made using chromium  $K\alpha$  radiation although iron and copper targets were used on occasions during the investigation.

## **Experimental Results**

*Mo-Ni-System:* The most recent comprehensive investigation of the Mo-Ni system was made by Ellinger<sup>4</sup> in 1942; the diagram as shown in the American Society for Metals Handbook is based on his work. The work done on the system in this investigation substantiated the general form of the diagram although some differences were observed. These are indicated by a comparison of Ellinger's diagram and Fig. 1, the latter showing the results of pertinent thermal analyses made in this research. It can be seen in Fig. 1 that the eutectic composition is



Fig. 1—Central region of Mo-Ni diagram based on thermal analysis data.

indicated to be approximately 57.5 pct Ni-42.5 pct Mo; this differs from Ellinger's value of about 54 pct Ni-46 pct Mo. Concomitant with the change in eutectic composition, a change in the liquidus curve was noted, as shown.

A second discrepancy was found in the peritectic temperature. The temperature as determined by thermal analysis is about 1350°C; the temperature given by Ellinger was 1370°C. The temperature of the eutectic reaction was found to be 1320°C, confirming Ellinger's results.

A third difference was found in the liquid composition in equilibrium with the molybdenum solid solution at the peritectic reaction temperature, 1350°C. Ellinger gave a value of about 48 pct Ni, whereas the best fit from this work is approximately 53 pct Ni.

It is difficult to decide which of the determinations is the more accurate. Ellinger made visual observations on solid samples as they were being heated, while the determinations reported here were developed from careful thermal analyses. Neither method can be claimed infallible, but it is felt that the values of the eutectic composition, the peritectic temperature, and the composition of the liquid at the peritectic temperature, which have been determined here, are more nearly correct than Ellinger's.

Recently, in unpublished work, the composition limits of the MoNi intermetallic compound have been questioned, but from the results observed in this research the equiatomic composition is to be included within the composition range, at 1250°C.

One further observation relative to the Mo-Ni system is that small additions of chromium raised the formation temperature of the compound  $Ni_{s}Mo$ . This point was not pursued in detail, but results leading to this observation were obtained in the pertinent thermal analyses. Presumably the  $Ni_{s}Mo$  field reaches a maximum temperature within the ternary system and then decreases, since the compound did not make its appearance in the 1250°C section of the ternary.

*Cr-Ni System*: Most of the results on the Cr-Ni system have been published.<sup>2</sup> Briefly, the diagram as presented showed a eutectoid reaction at about 1180°C with eutectoid composition of about 65 pct Cr-35 pct Ni; the phase above the eutectoid reaction was suggested to be a high temperature, face-centered cubic form of chromium labeled  $\beta$  Cr. In confirmation of this phase diagram and the mechanism of transformation in near-eutectoid alloys, one item of interest is presented.

It has been found that samples of near-eutectoid composition can transform from the high temperature  $\beta$  Cr phase to the low temperature  $\alpha$  Cr and  $\gamma$  Ni by means of an intermediate structure. This has been suggested previously.2 It has also been noticed that this transformation is strongly strainsensitive. One rather interesting aspect of this transformation is revealed in Fig. 2. Fig. 2a shows the X-ray diffraction pattern obtained with chromium radiation on a 60 pct Cr-40 pct Ni sample as quenched from 1250°C. The lines due to the  $\gamma$  Ni phase are present, plus the lines ascribed to the  $\beta$  Cr phase. Fig. 2b shows a pattern from the same sample after the surface had been lightly cold worked by polishing on fine emery paper. A shift in the  $\beta$ Cr lines can be noticed, while the  $\gamma$  Ni lines have almost disappeared as a result of the distortion.

At this point it becomes necessary to consider the movements of lines of the chromium solid-solution







Fig. 3—Constitution diagram of Cr-Mo system from the Metals Handbook, ASM.

phase in Fig. 2 and the structures responsible for these lines. The lines in Fig. 2b which are produced by the chromium phase no longer fit the pattern of a face-centered cubic structure because of the shifting in opposite directions which they have experienced. The pattern which they do fit, however, is that of a body-centered tetragonal structure; and this intermediate, transitional tetragonal structure is called  $\alpha'$  Cr. This follows of course because of the similarity between the body-centered cubic and body-centered tetragonal cells, and because the tetragonal structure apparently does collapse into the cubic structure under the appropriate conditions. It has been observed that the two  $\alpha'$  Cr lines tend to approach each other (indicating a decreasing c/a ratio) and merge to form the  $\alpha$  Cr (110) line of the normal body-centered cubic phase. In any event, as soon as the  $\beta$  Cr (200) line, for example, shifts (as long as the  $\beta$  Cr (111) line shifts a commensurate amount in the opposite direction), it can no longer be called the  $\beta$  Cr (200) line but becomes the  $\alpha'$  Cr (110). Similarly, the  $\beta$  Cr (111) line becomes the  $\alpha^\prime$  Cr (101) line upon shifting. And these  $\alpha'$  Cr lines ultimately become one  $\alpha$  Cr line as the structural changes are completed.

Fig. 2c shows the pattern taken from the same surface after the sample had been annealed 30 min in boiling water. The only evident changes are the re-appearance of the  $\gamma$  Ni (111) line and a slight shift in the  $\alpha'$  Cr lines. In Fig. 2d, the same sample, after being annealed an additional 15 min in molten lead at 360°C, shows an interesting development. The  $\alpha'$  Cr (110) line has split off an additional line. A similar effect is not noticeable in the (101) line mainly because the specimen was oriented so as to maximize the (110) line and the effect there. In Fig. 2e the split of the line becomes more evident, and one leg of the diffraction line has practically resumed the  $\beta$  Cr (200) position, while the other leg is well on its way toward assuming the  $\alpha$  Cr (110) position. This seemingly indicates that on relatively low temperature annealing the intermediate phase follows two tendencies: 1—to transform in part to the low temperature  $\alpha$  Cr form, and 2—to revert to the undistorted high temperature  $\beta$  Cr form.

Cr-Mo System: The Cr-Mo system has been considered to consist of a complete series of solid solutions with a minimum in the liquidus curve near the chromium end of the system (see Fig. 3, which is from the 1948 American Society for Metals Handbook). Since the work on the Cr-Ni system had revealed that a transformation in pure chromium ex-

isted, it seemed advisable to examine the Cr-Mo binary more closely for evidence of the transformation in this system.

The point data from thermal analyses are shown in Fig. 4. These results indicated that the minimum in the liquidus curve is at a higher temperature and at a higher chromium composition than had previously been held. The minimum appears to be at about 1860°C and at a composition of about 80 wt pct Cr. This agrees extremely well with the earlier



Fig. 4—Some results of thermal analyses in the Cr-Mo system showing the liquidus for the system. Solid-state reaction temperatures are developed from both heating and cooling curves.

work of Potter, Putnam, and Grant,<sup>\*</sup> whose thermal analysis data for the liquidus are shown in Fig. 5.

It will be noted in Fig. 4 that reactions are indicated in the solid state. A satisfactory explanation of these points is not easily advanced. It should be noted further that the points shown in Fig. 4 were developed from both heating and cooling curves so that they cannot be imputed to nonequilibrium cooling conditions. Because of the presence of the points under the minimum of the liquidus it is difficult in this instance to see how these particular points can be connected in any way with the solidification or melting processes. Though the connection is not clear, they are considered to be derived from the transformation detected in the pure chromium.



Fig. 5—Portion of the Cr-Mo liquidus from Putnam, Potter, and  $\operatorname{Grant.}^3$ 



Fig. 6—1200°C section of the Cr-Mo-Ni system as developed by Rideout et al."

A phase diagram for the Cr-Mo system which conforms to the thermal analyses and includes the chromium phase change is not easily constructed, nevertheless, it is clear that the Cr-Mo phase diagram as previously drawn (Fig. 3) cannot be considered to be complete or correct.

While many efforts were made to utilize the data to determine the diagram below the liquidus, all of them had a number of weaknesses. The data are thus presented without interpretation except for the drawing in of the liquidus surface showing the minimum in agreement with the liquidus of Potter, Putnam, and Grant. Cr-Mo-Ni System: The scope of this portion of the investigation was to determine the liquidus surface of the Cr-Mo-Ni system as well as the 1250°C section. The examination of the binary systems was wider in scope, but only to afford an understanding of the conditions existing at 1250°C and above in the ternary system.

1250°C Section: Several previous investigations in this system have been made but the most pertinent one is that of Rideout, et al.<sup>°</sup> The presence in this system of the  $\sigma$  phase had first been reported by Putnam, Grant and Bloom<sup>°</sup> and also by Rideout et al.,<sup>°</sup> who also reported another ternary compound. This latter compound, of unidentified crystal structure, was called the "P" phase. These authors developed a portion of the 1200°C section of this system as shown in Fig. 6. The 1250°C section as developed in the present investigation is shown in Figs. 7 and 8, in weight percent and atomic percent, respectively.

Except for the region adjoining the Cr-Ni system the diagrams are fairly similar in outline and broadly indicate: 1—that the  $\sigma$  phase field diminishes with increasing temperature, and 2—that the ternary intermetallic compound *P* moves toward the Mo-Ni binary with increasing temperature. There are significant differences, however, in the extent of the  $\sigma$  fields.

The existence of the *P* phase was corroborated mainly on the basis of X-ray diffraction results, but a microstructure, one of many examined, of interest in this connection is shown. The diffraction lines as developed in this work are given in Table I in conjunction with the values of Rideout et al. (Some of the lines given by them but missing here may be  $\beta$  lines.) These values were obtained from powdered specimens of alloys which had been held



Fig. 7—1250°C section of the Cr-Mo-Ni system showing the heats which were used to determine the section. Values are in weight percent.



Fig. 8—Same 1250°C section as in Fig. 7, but with values in atomic percent.

for over 100 hr at  $1250^{\circ}$ C before powdering. The powders were then sealed in Vycor capsules and placed in a furnace at  $1250^{\circ}$ C, held there for 3 min and air cooled. Unfortunately the cooling took about 30 sec, and since the powder samples did not give exactly the same results as the lump samples, the method has been outlined. It was concluded that the cooling rate was not sufficiently fast for the powders to maintain the  $1250^{\circ}$ C equilibrium structure. The main difference was in the indicated location of the *P* phase; the powder samples indicated the *P* field to be at a slightly higher chromium content.

This shifting of the *P* phase field with temperature is further indicated by the microstructure of the as-cast 2 pct Cr-61 pct Mo-37 pct Ni alloy shown in Fig. 9. X-ray results show that at  $1250^{\circ}$ C the alloy consisted only of the  $\delta$  phase, but the ascast microstructure shows four phases to be present. These are identified provisionally as being  $\alpha$  solid

Table I. 20	Values	of	Lines	of	₽	Phase	Using	Chromium	Radiation
			and	Var	۱a	dium F	ilter		

Values from Rideout et al. <sup>5</sup>	Values from Heat 61, This Investigation	Values from Rideout et al. <sup>5</sup>	Values from Heat 61, This Investigation
51.08	50.7	66.72 66.16	66.7 67.1
57.38	57.4	67.70	
58.72 59.96	58.2		68.1 68.65
62.80 63.4	62.85	70.28 72.88	72.7
64.6	64.7	73.52	
65.86 65.94	65.8 66.1	74.14 77.38	74.0 77.4

solution Mo in the center of the crosses, P phase surrounding the  $\alpha$  Mo,  $\delta$  phase surrounding the P phase, and the matrix which is a eutectic of  $\delta$  and  $\gamma$  Ni. The identification of the P and the  $\delta$  phases is of course difficult and is based in part on X-ray considerations which indicate that both phases are present.

This order of solidification leads to the conclusion that at a temperature of 1250 °C the *P* phase extends even closer to the Mo-Ni binary. Extrapolating this trend to lower temperatures would mean that the *P* 



Fig. 9–2 pct Cr-61 pct Mo-37 pct Ni alloy as cast. The roughened material in the center of the crosses is  $\alpha$  Mo surrounded by the P phase, which is in turn surrounded by the  $\delta$  phase. The matrix is a eutectic consisting of  $\delta$  phase and  $\gamma$  Ni. Electrolytic polish and etch. X750. Area reduced approximately 40 pct for reproduction.



Fig. 10— $\sigma$  phase parameter as a function of varying Cr-Mo composition at a constant 30 atomic pct Ni, at 1250°C.

phase would extend into the ternary system, and this is borne out by comparison of the two diagrams in Figs. 6 and 7.

In the central area of the  $1250^{\circ}$ C section are shown the ternary  $\sigma$  phase boundaries. From Fig. 7 it can be seen that the field has a rather long, slender shape. When plotted in atomic percent (Fig. 8) the field orients itself fairly closely along a line of constant nickel content, this axis being at about 32 pct Ni. Thus it can be considered that the nickel atoms are present in a proportion of about onethird, while the chromium and molybdenum proportions vary over a rather wide range. This is thought to be not without significance, particularly since the width of the field at this temperature in terms of nickel content is so restricted.

From theoretical considerations' there is reason to suspect that  $\sigma$  phase could form in binary Ni-Cr system at a composition near 67 pct Cr-33 atomic pct Ni, and this is substantiated by the position and shape of the  $\sigma$  phase field in the ternary system. Extensive tests over a wide range of compositions, temperatures and long holding times, however, failed to produce  $\sigma$  in the binary Cr-Ni alloys. Apparently molybdenum has a powerful effect of promoting  $\sigma$  formation as it is substituted for chromium.

Fig. 10 shows the variation of the average of the d values of six of the strongest lines in the  $\sigma$  phase pattern plotted as a function of chromium and molybdenum contents under the assumption that the nickel content is constant at 30 atomic pct. There is a near-linear relationship indicated, considering the scatter of the heats.

An additional point of interest is that the  $\sigma$  phase in this system is considered to form directly from the liquid through a ternary peritectic reaction; and the elongated shape of the field assumes added interest because of the proximity of the 1250°C section to the peritectic temperature. This will be discussed in further detail subsequently.

The work in the Cr-Ni binary system resulted in the acceptance of a eutectoid reaction in this system. This must of course be fitted into the ternary system. As was mentioned in the discussion of the Cr-Ni binary, the experimental difficulties involved in studying the high temperature phase were rather formidable. The presence of molybdenum in appreciable amounts does not, unfortunately, increase the ease with which the high temperature chromium phase can be retained.

From the study of the X-ray results and the pertinent microstructures it can be definitely established that the two-phase field,  $\gamma$  Ni plus  $\alpha$  Cr, is the one which exists at 1250°C and not the alternative possibility,  $\sigma$  plus  $\beta$  Cr. Further, the extent of the three-phase field,  $\gamma$  Ni plus  $\alpha$  Cr plus  $\sigma$ , can be laid out approximately by reference to the relevant alloys; the same applies to the two-phase field,  $\gamma$ Ni plus  $\alpha$  Cr. Unfortunately the fields involving the  $\beta$  Cr phase cannot be laid down with accuracy. To illustrate this, two sample X-ray patterns are shown in Fig. 11 and are compared with a pattern of the two lower temperature phases,  $\gamma$  Ni and  $\alpha$  Cr (Fig. 11a). Fig. 11b is from a 63.5 pct Cr-3.5 pct Mo-33 pct Ni alloy; here lines of the  $\gamma$  Ni phase and one line of the intermediate metastable  $\alpha'$  Cr phase are identified. It is deduced from this that at 1250°C the sample had consisted of  $\gamma$  Ni plus  $\beta$  Cr, and that during the quench, or in preparation, the  $\beta$  Cr phase transformed to the  $\alpha'$  Cr state. Fig. 11c is of a 66.5 pct Cr-3.5 pct Mo-30 pct Ni alloy; the lines present here are ascribed to the  $\alpha$  Cr and  $\alpha'$  Cr phases. However, to conform to other results it is necessary to conclude that at 1250°C this sample was mostly  $\beta$  Cr, but on cooling, or during preparation, the  $\beta$ Cr phase again had partially decomposed. Though these patterns and other similar patterns are not entirely satisfactory for delineating the fields at 1250°C, they do indicate conclusively that there







Fig. 12—Plot of liquidus temperatures and isotherms.



Fig. 13—Proposed system of high temperature invariant plane of the Cr-Mo-Ni system above 1250°C.



Fig. 14—Cooling curve of 9 pct Cr-79 pct Mo-12 pct Ni alloy. Time increases from right to left. The first change of slope is at about 2120°C, the second at about 2045°C.

does exist another phase at this temperature, located approximately as shown in Figs. 7 and 8.

The Liquidus Surface: The liquidus surface was developed from the liquidus temperatures as determined for each alloy by thermal analysis. The liquidus temperatures were taken to be the average of the cooling and heating values obtained at rather slow rates of temperature change. It was determined experimentally that for the particular experimental setup used, a cooling rate of 10°C per min would yield data with an accuracy commensurate with the accuracy of the W-Mo thermocouple. At more rapid cooling rates the accuracy became poorer. In actual practice cooling rates of about 5°C per min were maintained.

The liquidus surface as developed is shown in Fig. 12. No discontinuities are indicated in the isothermal lines, though in actuality some must exist. The minimum melting point found was about  $1275^{\circ}$ C in what is thought to be a ternary eutectic. The composition at this point is about 19 pct Cr-34 pct Mo-47 pct Ni. The maximum melting point found is that of pure molybdenum. There were no ternary compounds detected which melted with open maxima.

System of Invariant Planes: The development of the system of invariant planes existing about 1250°C has been undertaken and a construction developed which is at least compatible with all the data available. Since extensive work was not attempted involving reactions occurring between 1250°C and the liquidus temperatures, the synthesis must be accepted as somewhat provisional. The system as developed is reproduced in Fig. 13. In this construction the triangles and quadrilaterals representing the invariant planes are to be understood as being schematic rather than definitive. The scheme is reproduced mainly to assist others who may contemplate further exploration of the system.

It will be noted that there is no three-phase field coming down on to the invariant plane at 1500°C denoting the 3/1 (peritectic) reaction whereby the  $\sigma$  phase is formed. The phases which would be in coexistence in this field are the liquid plus  $\alpha$  plus  $\beta$ phases. This field could be considered as originating in the Cr-Mo binary system and then moving with falling temperatures to the location as shown, but the thermal analyses and as-cast microstructures did not substantiate such a construction. The solution which did present itself, but is not shown because the evidence did not seem to warrant such a drastic innovation, was that there existed a threephase field,  $\alpha$  plus  $\beta$  plus liquid, which was based on a reaction occurring at very high temperatures in the Mo-Ni system. This would necessitate a high temperature transformation in molybdenum similar to the one which apparently occurs in chromium. In support of this hypothesis a cooling curve of an

alloy of 9 pct Cr-79 pct Mo-12 pct Ni is shown in Fig. 14. The arrest occurring at about 2045°C indicates a more complicated solidification process than is involved in a mere liquidus-solidus type of solidification.

It is because of this indicated solid state change in the above alloy and the solid state change indicated with Cr-Mo binary system that no attempt was made to introduce a phase diagram, other than the liquidus curve, for the Cr-Mo binary (Fig. 4).

#### Summary

1—The investigation of the Mo-Ni system has resulted in some changes in the phase diagram in the regions of the eutectic and peritectic reactions.

2—The investigation of the Cr-Ni system has developed interesting phenomena concerning the intermediate structure associated with the eutectoid reaction. It has been shown that the retained high temperature phase can be decomposed by annealing or cold working near room temperature.

3—It has been concluded that the Cr-Mo system as presently accepted is incorrect, and while a definite revision has not been developed, suggestions have been advanced for possible changes of the diagram.

4—The 1250°C section of the Cr-Mo-Ni system has been developed, showing the rather interesting shape of the  $\sigma$  phase field at this temperature. The existence of another ternary compound called the *P* phase has been corroborated.

5—The liquidus surface of the ternary has been outlined.

6—A possible system of invariant planes for the ternary system Cr-Mo-Ni is suggested.

#### Acknowledgments

The authors wish to express thanks to Dr. J. W. Putnam for assistance and the Bureau of Aeronautics under whose sponsorship the work was performed.

## References

<sup>1</sup>D. S. Bloom, J. W. Putnam, and N. J. Grant: Melting Point and Transformation of Pure Chromium. *Trans.* AIME (1952) **194**, p. 626; JOURNAL OF METALS (June 1952).

<sup>2</sup>D. S. Bloom and N. J. Grant: Chromium-Nickel Phase Diagram. *Trans.* AIME (1951) **191**, p. 1009; JOURNAL OF METALS (November 1951).

<sup>8</sup> J. W. Putnam, R. D. Potter, and N. J. Grant: The Ternary System Chromium-Molybdenum-Iron. *Trans.* ASM (1951) **43**, p. 824.

<sup>4</sup> F. H. Ellinger: The Nickel-Molybdenum System. Trans. ASM (1942) **30**, p. 607.

<sup>8</sup>S. Rideout, W. D. Manley, E. L. Kamen, B. S. Lement, and P. A. Beck: Intermediate Phases in Ternary Alloy Systems of Transition Elements. *Trans.* AIME (1951) **191**, p. 872; JOURNAL OF METALS (October 1951).

<sup>6</sup>J. W. Putnam, N. J. Grant, and D. S. Bloom: Sigma Phase in Chromium-Molybdenum Alloys with Iron or Nickel. Symposium on the Nature, Occurrence and Effects of Sigma Phase. ASTM, Spec. Pub. 110, June 1950.

<sup>7</sup>D. S. Bloom and N. J. Grant: Regarding Sigma Phase Formation. *Trans.* AIME (1953) **197**, p. 88; JOURNAL OF METALS (JANUARY 1953).

### 268—JOURNAL OF METALS, FEBRUARY 1954