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UNITED STATES
DEPARTMENT OF THE INTERIOR
J. A. KRUG, SECRETARY

BUREAU OF MINES
JAMES BOYD, DIRECTOR



REPORT OF INVESTIGATIONS

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# A TENTATIVE TITANIUM-NICKEL DIAGRAM[1]

By J. R. Long,[2] E. T. Hayes,[3] D. C. Root,[4] and C. E. Armantrout[4]

The Federal Bureau of Mines has pioneered the work of preparing ductile titanium on a large scale and has also determined the basic properties of this new and most interesting metal. A number of reports (1, 2, 3, 4, 5) have already been published, and considerable interest has been aroused in a number of industrial and research laboratories. Some of these laboratories have also published results of their work on the pure metal (6, 7).

Although the properties of titanium itself are quite promising, it is apparent that considerable improvement may be expected by alloying titanium with other metals. That is, pure metals in general have shown relatively large improvements in properties when alloyed with other metals and titanium is not considered to be an exception to the rule: Therefore, the emphasis of the investigations now under way in the Federal Bureau of Mines Laboratories has been placed on the study of the alloys of titanium, particularly the titanium-rich alloys. While the main interest is in the properties of such alloys, proper direction and evaluation of the work require at least a rough outline of the phase boundaries of the alloy systems involved.

One of the alloy systems under investigation is the titanium-nickel system. Although there are some data in the literature on the phase diagram of these alloys, the work reported has been conducted on quite impure titanium and is therefore apt to be misleading. Wallbaum (9) has published a diagram concerned with the nickel-rich alloys but presents no data on the titanium-rich portion of the system. Accordingly, it was necessary to study the phase relationships in titanium-nickel alloys, and while this study was by no means exhaustive and the impurities present in the titanium have affected the results significantly, enough data have been obtained to permit an estimation of the general features of the titanium-nickel diagram up to 40% nickel. This paper presents the data obtained thus far, and although they are admittedly incomplete, they are being reported at this time because of the great interest in the titanium-alloy works being conducted by the Bureau.

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1/ Work on manuscript completed December 1948. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Report of Investigations 4463."

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The major portion of the data is concerned with delineation of the solid-phase equilibria, particularly the beta titanium solid solution and its eutectoidal decomposition. Little attempt was made to determine the liquidus or the solidus lines at very high temperatures, but the data do allow a tentative approximation of their positions in the range from 1,200° C. down to 960° C.

## PREPARATION OF ALLOY

The titanium used was prepared at the Boulder City Experiment Station of the Federal Bureau of Mines by the usual method, and a representative analysis of this metal is given in table 1. It should be noted that, while the iron, magnesium, silicon, and hydrogen contents given are quite well established, the oxygen, and possibly the nitrogen, contents are somewhat uncertain. These gases have been determined by various laboratories with considerable spread in the values reported, but it is believed that the amounts noted are a fair approach to the true value; they are, however, subject to revision. Considerable work is being conducted on vacuum fusion methods, and more consistent results should be obtained in the near future. The nickel powder was a high-grade, hydrogen-reduced powder. Its representative analysis is also given in table 1. Before use the nickel was given a hydrogen treatment to avoid the effects of oxidation of the powder in storage.

TABLE 1. - Chemical analysis, percent

| Material | Fe | Co | $O_2$ | C | Mg | Ca | Si | $H_2$ | Insol. | Mesh |
|---|---|---|---|---|---|---|---|---|---|---|
| Ni ..... | 0.25 | 0.56 | - | 0.06 | - | - | - | - | 0.2 | -200 |
| Ti ..... | .15 | - | 0.1-0.2 | - | 0.30 | 0.036 | 0.005 | .7 | - | -35 |

Because of the contamination of titanium that would be introduced by melting, the alloys were prepared by powder-metallurgy methods. In general, the powders were hand-mixed in the proportions required to produce the desired composition, and, after adding 3 to 4 cc. of benzene to prevent segregation of the fines, they were carefully loaded in a steel die and pressed at 50 tons per square inch, forming compacts approximately 3/8- by 1-1/2- by 3-inches in size. After drying, the compacts were reweighed and measured to permit determination of shrinkage and weight loss on sintering. The sintering was carried out in a vacuum of $1 \times 10^{-4}$ mm. of mercury. Up to and including the 10 percent alloy a sintering temperature of 1,000° C. was used. As the alloys containing more nickel melted at this temperature in the preliminary trials, these alloys were first sintered at 800° C. Later it was found that 900° C. was a safe limit, and the additional high nickel alloys required were sintered at 900° C. The nominal and actual nickel contents of the alloys prepared and used in this work are listed in table 2. Iron content was determined on a number of the alloys and is also given. These values however are inaccurate because of iron contamination in preparing the samples. In general, the high-nickel alloys show high iron content. This is considered to be caused by the relatively high hardness of these alloys which lead to iron pickup on sampling. The results on the low-nickel alloys and on several high-nickel alloys in which the samples were more easily prepared by crushing indicate an iron content of 0.18 to 0.25 percent is more nearly correct.

TABLE 2. - Chemical composition of Ti-Ni alloys, percent

| Alloy No. | Nominal Ni | Comp. Ti | Chem. Ni. | Analysis Fe | Alloy No. | Nominal Ni | Comp. Ti | Chem. Ni | Analysis Fe |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.0 | 100.0 | - | 0.22 | 33 | 8.0 | 92.0 | 7.90 | 0.56 |
| 2 | .5 | 99.5 | 0.52 | - | 34 | 8.0 | 92.0 | 7.85 | - |
| 3 | .5 | 99.5 | .40 | - | 35 | 9.0 | 91.0 | 8.45 | - |
| 4 | .5 | 99.5 | .49 | - | 36 | 10.0 | 90.0 | 9.45 | - |
| 5 | 1.0 | 99.0 | .92 | - | 37 | 10.0 | 90.0 | 8.15 | .48 |
| 6 | 1.0 | 99.0 | .82 | - | 38 | 10.0 | 90.0 | 9.20 | .30 |
| 7 | 1.0 | 99.0 | .86 | - | 39 | 10.0 | 90.0 | 9.93 | .38 |
| 8 | 2.0 | 98.0 | 1.70 | .22 | 40 | 10.0 | 90.0 | 9.93 | .62 |
| 9 | 2.0 | 98.0 | 1.67 | - | 41 | 12.0 | 88.0 | 11.1 | - |
| 10 | 2.0 | 98.0 | 2.00 | - | 42 | 12.0 | 88.0 | 11.5 | .61 |
| 11 | 2.0 | 98.0 | 2.12 | - | 43 | 14.0 | 86.0 | 13.2 | - |
| 12 | 2.0 | 98.0 | 1.82 | - | 44 | 15.0 | 85.0 | 14.2 | - |
| 13 | 3.0 | 97.0 | 3.0 | - | 45 | 15.0 | 85.0 | 12.8 | - |
| 14 | 4.0 | 96.0 | 3.7 | .33 | 46 | 15.0 | 85.0 | 14.4 | .37 |
| 15 | 4.0 | 96.0 | 3.9 | - | 47 | 16.5 | 83.5 | 15.4 | - |
| 16 | 4.0 | 96.0 | 3.50 | - | 48 | 17.0 | 83.0 | 16.7 | .32 |
| 17 | 4.0 | 96.0 | 3.82 | - | 49 | 18.0 | 82.0 | 17.4 | - |
| 18 | 5.0 | 95.0 | 4.70 | - | 50 | 19.0 | 81.0 | 18.5 | - |
| 19 | 5.0 | 95.0 | 4.35 | - | 51 | 20.0 | 80.0 | 18.4 | - |
| 20 | 5.0 | 95.0 | 4.75 | - | 52 | 20.0 | 80.0 | 17.05 | .28 |
| 21 | 5.5 | 94.5 | 5.4 | - | 53 | 20.0 | 80.0 | 19.0 | - |
| 22 | 6.0 | 94.0 | 5.75 | - | 54 | 22.5 | 77.5 | 20.7 | - |
| 23 | 6.0 | 94.0 | 5.9 | - | 55 | 22.5 | 77.5 | 22.25 | .18 |
| 24 | 6.0 | 94.0 | 5.63 | - | 56 | 25.0 | 75.0 | 23.0 | - |
| 25 | 6.0 | 94.0 | 5.54 | - | 57 | 25.0 | 75.0 | 24.75 | - |
| 26 | 6.5 | 93.5 | 6.35 | - | 58 | 30.0 | 70.0 | 28.7 | - |
| 27 | 6.5 | 93.5 | 6.35 | - | 59 | 30.0 | 70.0 | 25.5 | .25 |
| 28 | 7.0 | 93.0 | 6.72 | - | 60 | 35.0 | 65.0 | 34.4 | - |
| 29 | 7.0 | 93.0 | 6.75 | - | 61 | 37.5 | 63.5 | 36.5 | - |
| 30 | 7.5 | 92.5 | 7.2 | - | 62 | 40.0 | 60.0 | 39.8 | - |
| 31 | 8.0 | 92.0 | 7.55 | - | 63 | 40.0 | 60.0 | 39.75 | .22 |
| 32 | 8.0 | 92.0 | 7.75 | 0.65 | 64 | 45.0 | 55.0 | 43.7 | - |

## TREATMENT OF ALLOYS

In the initial work small specimens were cut from the sintered compacts and heat treated at various temperatures for varying lengths of time to determine the phase relationships. However, it was found that the microstructures of these sintered and heat treated samples were definitely nonhomogeneous and that the large void spaces interfered greatly with interpretation of the structures. This was especially true of the high nickel alloys and was very pronounced in compositions above 10 percent nickel. The relatively large grain size of the titanium powder (-35 mesh) compared to that of the nickel powder (minus 200-mesh) undoubtedly played a significant part in accentuating these difficulties. Finer grinding of the titanium would be of little help as fine titanium powder has been found to be harder and less ductile than the normal powder because of a greater tendency to oxidize in processing. While cold-working the sintered compacts to close voids and help break up segregation

would be of some assistance, the sintered alloys containing more than 5 percent nickel were too brittle to take an appreciable amount of cold work before breaking up.

One technique adopted to circumvent these difficulties consisted of enclosing the sintered compacts in iron sheaths and hot working at elevated temperatures. This technique has been used for protecting titanium, zirconium and many other metals, worked at high temperatures. Van Arkel and his coworkers, as well as Kroll and others, have used it to advantage. In our case, the sheaths were formed of 1-1/4-inch seamless tubing forged to fit the 3/8- by 1-1/2- by 3-inch compacts. The ends were closed by inserting iron plugs and welding. Care was taken to clean the interior of the sheath before inserting the titanium-nickel alloy compacts and making the final weld. Since some oxidation of the titanium could take place during the final closure, waste pieces of titanium were usually placed on the sintered compact, between it and the iron plug, to take up oxygen during the welding. However, to be certain that possible oxidation of these ends would not affect the results of this work, the ends of the compact were discarded, and only specimens cut from the center portion of the compact were used.

The general procedure followed consisted of sheathed rolling of sintered compacts at temperatures ranging from 800° to 950° C. The higher temperatures were used whenever it was felt they would be of assistance in producing single-phase structures. After soaking in the furnace at the rolling temperature, the compacts were water-quenched. These compacts were readily removed from the sheaths by cutting off the ends and opening the side of the sheath. There was no tendency for the compact to stick to the iron; and the alloys exhibited bright, fairly smooth surfaces, except where air leaked into the sheath through cracked or imperfect welds. Discolored compacts were discarded, since contamination by oxygen and nitrogen was known to have significant effects. Structural effects at the surfaces of the compacts indicated that some iron was absorbed on the surface. These were, however, confined to the contact faces and were disregarded in evaluating the microstructures of the heat-treated specimens. To void spaces of these compacts were substantially closed up and great improvements in structural homogeneity were noted as a result of this treatment.

For subsequent heat treatment, samples cut from these rolled compacts were sealed in quartz tubes, which were evacuated and back-filled with helium. They were then heated to various temperatures for varying lengths of time and cooled in several ways. Some were quenched in water, some in iced brine, and others air- or furnace-cooled. The temperature of treatment and cooling method chosen in each case, depended on the type of data desired.

A second procedure also used consisted of rerolling portions of the sintered and rolled compacts at the temperature levels under investigation. That is, portions of the compacts rolled at 800° to 950° C. were again sealed in iron containers and rolled at temperatures ranging from 700° to 1,000° C., held at this temperature for 1 hour or more, and then water-quenched. These samples were generally given 50 to 75 percent reduction in thickness, with frequent reheating to maintain the temperature. It was felt that this method of operation

would produce the quickest approach to equilibrium conditions at the rolling temperature, especially if the working was substantial in amount and if the specimens were soaked after rolling. While it was not possible to control the rolling temperature exactly because of loss of heat during rolling etc., this was not considered significant as long as the temperature drop was not excessive and the specimens were soaked at controlled temperatures immediately afterward. Specimens rolled at 700° to 800° C. were soaked up to 48 hours after the final pass through the rolls. In the range 800° to 850° C. the soaking time was usually 16 to 24 hours, and above 850° C. the soaking time was reduced to 1 hour. Specimens so treated showed excellent structural consistency. The microstructures were considerably improved over those obtained by the sintering and rolling and the alloys are believed to have closely approached equilibrium condition for the temperature levels involved.

A third procedure also used in this work involved an entirely new method of consolidating the powder compacts. This method, applicable to many other metals as well as titanium and its alloys, will be described elsewhere and need not be discussed in detail here. It consists of sheath-rolling green dehydrogenated powder-metal compacts. That is, pressed but not sintered compacts were sealed in iron sheaths, heated for an hour or so at 850° to 950° C., and rolled with frequent reheating between passes through the rolling mill. These rolled compacts were then rerolled and treated in the same manner as in the second procedure. The alloys in general showed a decided improvement in structural homogeneity indicating that very rapid diffusion had taken place between the titanium and nickel during the initial hot working. In fact, this method of alloy preparation is considered to be the most desirable for producing sound structurally homogeneous alloys.

## Effect of Oxygen

In the early stages of this work several discrepancies were encountered which indicated that the alloys were not behaving as simple binary alloys. The alphabeta transformation was found to be completed in alloys containing a few percent nickel only when they were heated above 935° C., while the reverse beta-alpha transformation was not completed in any of the alloys until they were cooled below 775° C. This suggested that nickel was both raising and lowering the 875° C. alpha-beta transformation point of titanium and would have been a rather odd behavior. It was, however, also found that many alloys consisted of three phases in certain temperature ranges and that the structures obtained were reproducible. From this it was apparent that the alloys were more complex than simple binary alloys and were behaving more on the order of a ternary system. Consideration of the behavior of the titanium treated in the same manner as the alloys and of other data available from the investigation in progress on the titanium-oxygen system indicates that oxygen has a very significant effect on the titanium nickel alloys. Approximately 0.1 to 0.2 percent oxygen is known to be present in the titanium powder. Examination of a number of titanium-nickel alloys to which known amounts of oxygen have been added also bears out this conclusion. While nitrogen and hydrogen are also present, the nitrogen content is quite low, and the hydrogen is not carried through to the alloys. Iron is also present but the amount also low, and other studies also in progress suggest that iron behaves like nickel and lowers the the alpha-beta transformation. It is therefore believed that the oxygen content of the titanium is responsible for these effects.

Although the Bureau's work on the titanium-oxygen system is not yet complete the data indicate that oxygen raises the transformation point quite rapidly, and this, together with the tendency for nickel to lower the transformation, would explain the discrepancies noted. The alloys should therefore be thought of as three-component alloys and the diagram prepared from the structural data considered a quasi-binary section of the titanium-nickel-oxygen system rather than a simple binary. This however does not detract from the usefulness of the data, since they do permit an estimation of the true phase relationships in the titanium-nickel system, complete delination of which must wait until the alloys can be prepared without contamination.

## Determination of Solidus

In the course of sintering the high-nickel alloys, melting was encountered at 1,000° C. with alloys containing 15 percent nickel. It therefore became necessary to determine the solidus for the composition range under investigation so that undesired melting could be avoided. For this purpose samples were sealed in quartz tubes in helium under low pressure, heated to the temperatures in question and water-quenched. The occurrences or absence of melting was determined by micro-examination of these specimens. This method of detecting melting is quite sensitive in single-phase alloys and, while not as sensitive, still satisfactory for two-phase alloys. Representative structures encountered in these melting studies are to be found in figures 2 to 7. The Widmanstatten structure of figure 2 is quite typical of titanium and the alloys of low nickel content. It is apparently the result of the transformation of beta to alpha titanium during the quench. No signs of melting are visible in figure 2, but very definite indications of melting are to be found in figure 3. Likewise figure 4 shows only a trace of melting in the 11.1 percent nickel alloy, while in figure 5 (13.2 percent Ni) it is apparent that general melting occurred at the quenching temperature. The ground mass of these two structures consists of untransformed beta titanium solid solution instead of the Widmanstatten structure. This is quite characteristic of alloys containing more than 10 percent nickel. Increasing nickel appears to stabilize the beta solution, and it then can be preserved by quenching. Partial melting is also evident in figure 6 (20.7 percent Ni at 990° C.) and general melting figure 7 (28.7 percent Ni at 990° C). The results of these tests are tabulated in table 3, where the alloys are listed by composition in three classifications, namely, no melting, partial melting, and general melting for the temperature levels examined. The data are also plotted in the diagram of figure 1.

The addition of nickel lowers the melting point of titanium very rapidly. The 6.72-percent alloy begins to melt at 1,200° C., and with higher nickel contents the solidus drops to 960° C. at about 12 percent nickel. This is a rather sharp drop from 1,745° C., the accepted melting point of titanium, and it is quite obvious that high melting point alloys are not to be found in this system. From 11.1 percent nickel on, the solidus appears to remain constant at 960° C., suggesting a eutectic or peritectic reaction at this temperature. Since there were definite areas of eutectic structure in several alloys at 30 to 35 percent nickel, and the estimates of the amount of melting that occurred are also in agreement, a eutectic has been indicated at 33 percent nickel and 960° C. X-ray data indicates the occurrence of a new phase between 39.8 and 43.7 percent nickel, and the eutectic horizontal is therefore extended to 41.5 percent nickel.

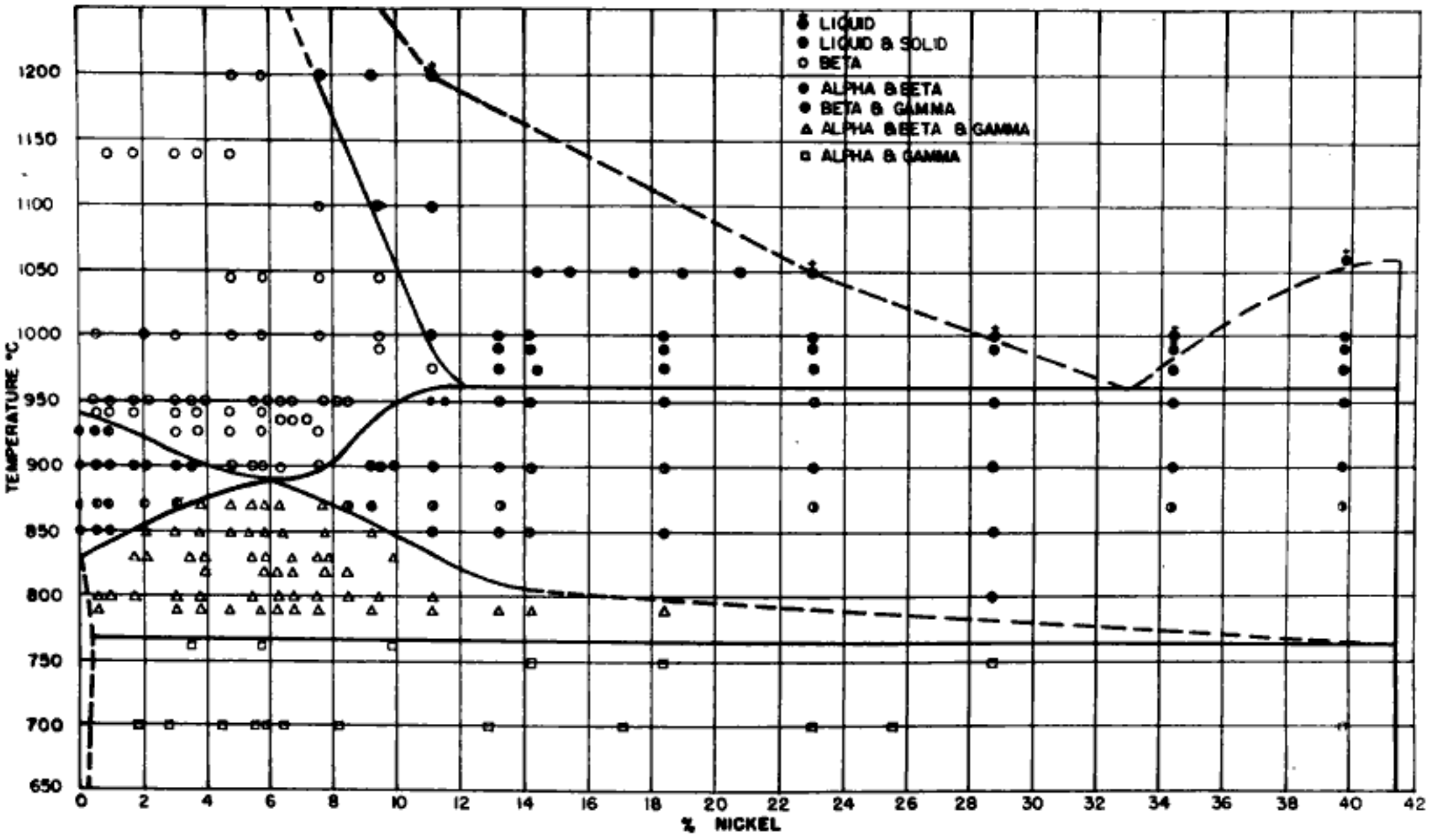


Figure 1. - Titanium-nickel quasi-binary diagram.

Figure 2. - Microstructure of 4.75 percent Ni alloy quenched from 1,200° C.; no melting has occurred at this temperature. X250

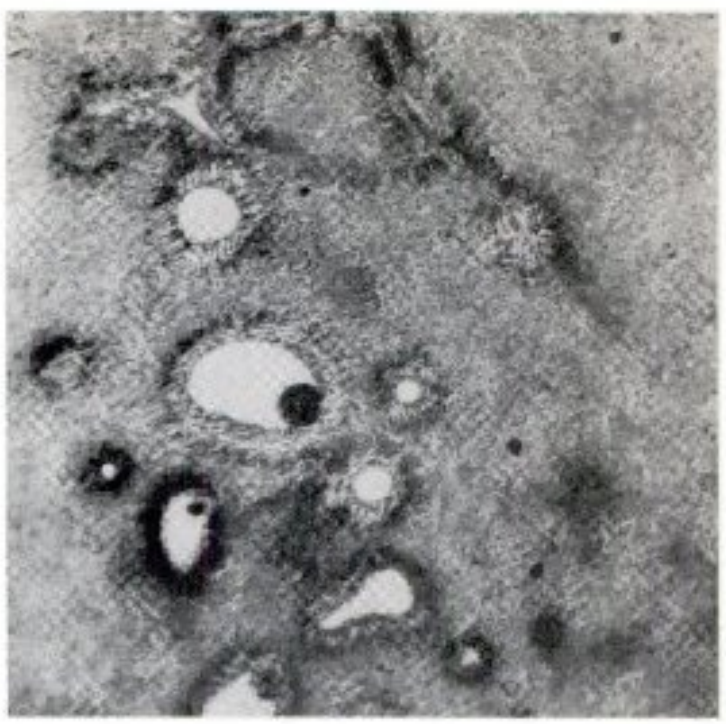

Figure 3. - Microstructure of 7.55 percent Ni alloy quenched from 1,200° C.; some melting has taken place. X250

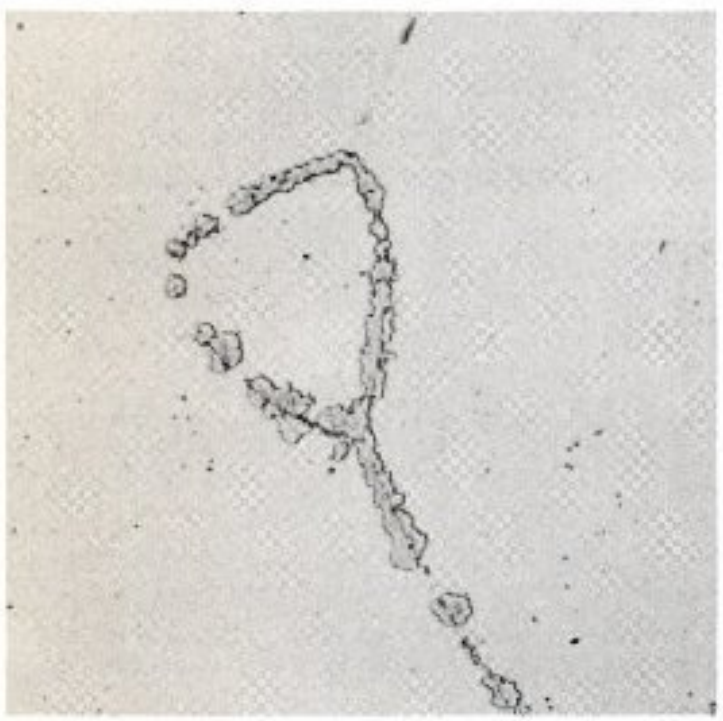

Figure 4. - Microstructure of 11.1 percent Ni alloy quenched from 1,000° C.; traces of melting in the grain boundaries. X250

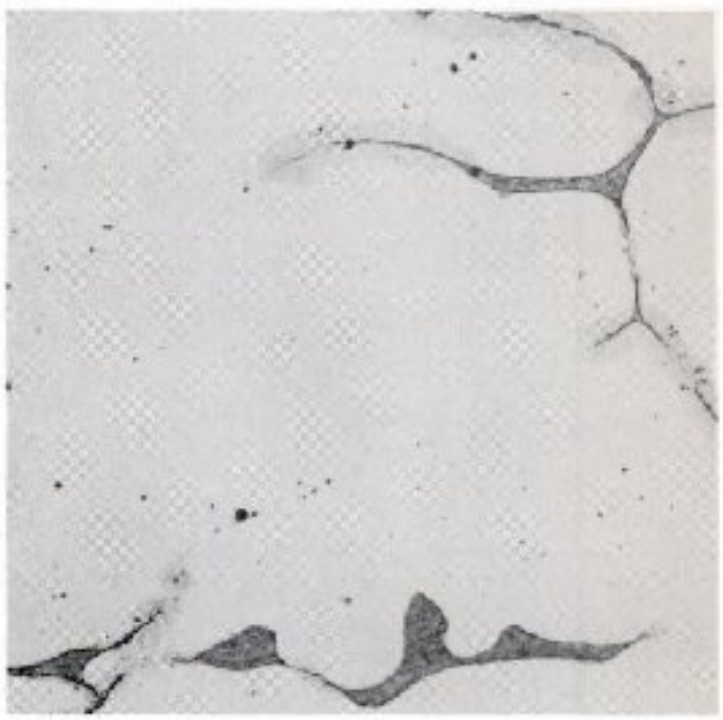

Figure 5. - Microstructure of 13.2 percent Ni alloy quenched from 1,000° C.; partial melting has occurred at this temperature. X250

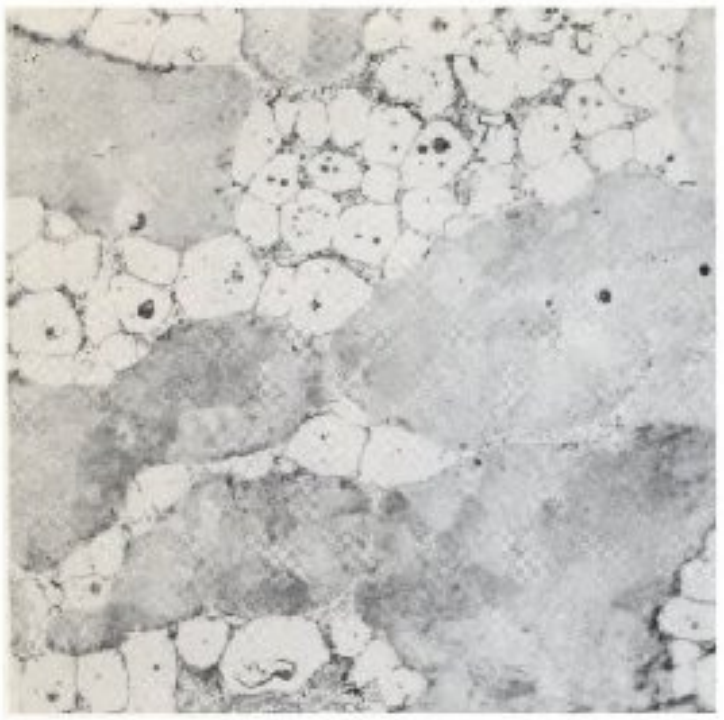

Figure 6. - Microstructure of 20.7 percent Ni alloy heated to 990° C.; partial melting has occurred and some eutectic formed on solidfication. X250

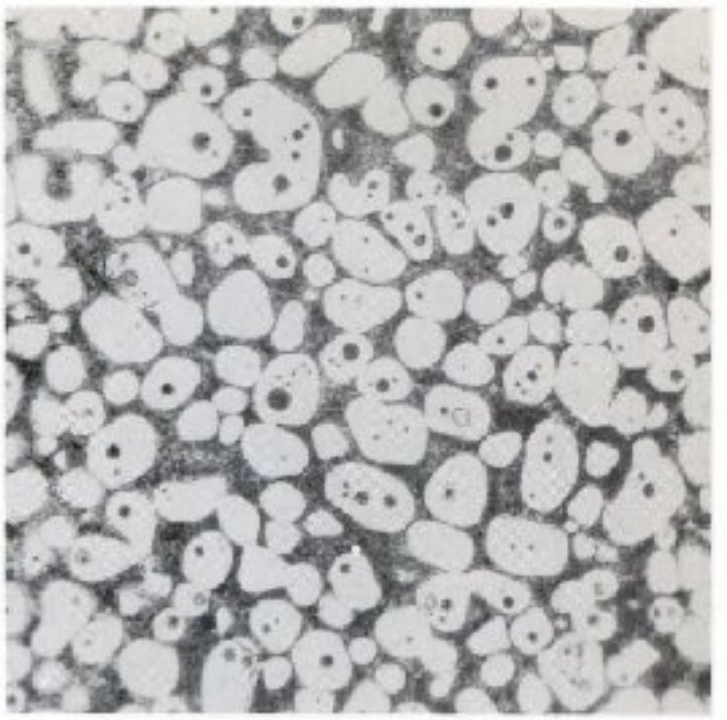

Figure 7. - 28.7 percent Ni alloy heated to 990° C.; general melting has taken place at this temperature. X250

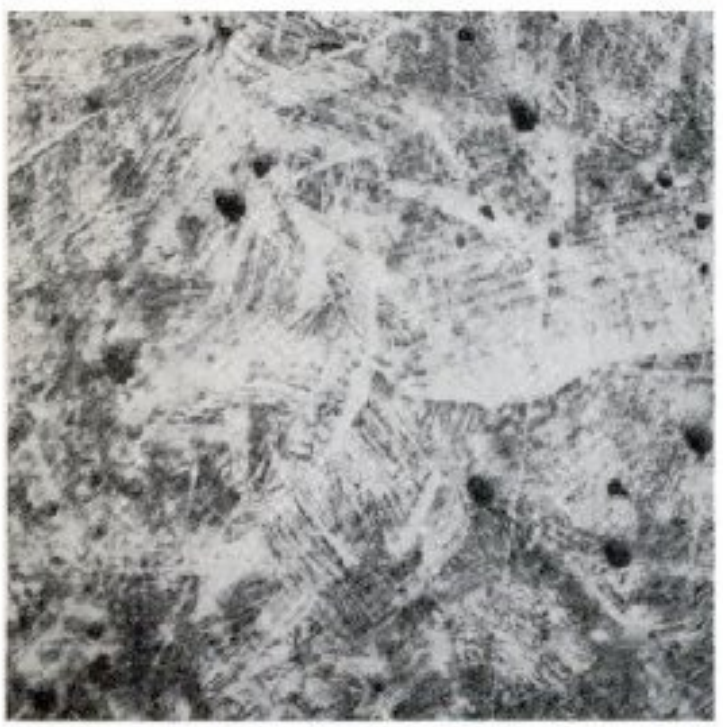

Figure 8. - Microstructure of 0.40 percent Ni alloy water-quenched from 950° C.; alloy was composed of beta solid solution at temperature. X100

Figure 9. - Microstructure of 0.92 percent Ni alloy water-quenched from 950° C.; alloy in beta field at temperature, structure typical of decomposition of beta on cooling. X250

TABLE 3. - Melting-point studies

| Temperature of treatment | Nickel content of alloys examined | | |
|---|---|---|---|
| | No melting | Partial melting | General melting |
| 1,200° C. | 4.75, 5.75 | 6.72, 7.55, 9.20 | 11.1 |
| 1,140° C. | 0.92, 1.7, 4.7, 3.0, 3.7 | - | - |
| 1,100° C. | 7.55 | 9.20, 11.1 | - |
| 1,060° C. | - | - | 39.8 |
| 1,050° C. | - | 14.4, 15.4, 17.4, 19.0, 20.7 | 23.0 |
| 1,045° C. | 4.7, 5.75, 7.55, 9.45 | - | - |
| 1,000° C. | 0, 0.49, 0.86, 2.0, 3.0, 3.7, 4.75, 5.75, 7.55, 9.2 | 11.1, 13.2, 14.2, 18.4 | 23.0, 28.7, 34.4, 39.8 |
| 990° C. | 9.45 | 11.1, 13.2, 14.2, 18.4, 20.7, 23.0 | 28.7, 34.4, 39.8 |
| 975° C. | - | 16.7, 17.4, 18.5, 19.0, 20.7, 23.0, 39.8 | - |
| 950° C. | No melting encountered in alloys up to 50 percent Ni | | |

## STRUCTURE OF SOLID PHASES

As previously noted, the beta form of titanium, stable above 875° C., cannot be preserved by quenching. Instead it decomposes, forming a Widmanstatten type of structure which X-ray diffraction patterns show to be entirely alpha titanium. Estimation of the presence of beta titanium at temperatures above its transformation point have therefore been based on the occurrence or absence of the Widmanstatten structure in quenched specimens. The low-nickel-content alloys behave in a similar fashion. Structures consisting of mixtures of the alpha and beta phases at a given temperature can be identified by the presence of the Widmanstatten and simple alpha structures in the quenched alloys. Those which are entirely beta at temperature will show only the Widmanstatten structure on quenching. Alloys with more than 5 percent nickel stabilize the beta solution and on quenching give a large grain structure which X-ray diffraction patterns show to be entirely beta titanium. Differentiation between the beta and beta-gamma fields is readily made because of the etching characteristics and mode of formation of the gamma. The gamma particles also stand in relief on polishing so that small amounts can be easily detected.

Table 4 gives the composition of the alloys found to lie in the beta field on quenching from temperatures between 1,200° and 900° C. No alloys were found to be entirely beta at the next lowest temperature. While most of these data are also plotted in figure 1, a number have been omitted from the chart for the sake of clarity.

TABLE 4. - Alloys in beta field

| Temperature | Composition of alloy |
|---|---|
| 1,200° C. | 4.75, 5.75 |
| 1,140° C. | 0.92, 1.70, 4.70, 3.0, 3.7 |
| 1,100° C. | 7.55 |
| 1,045° C. | 4.7, 5.75, 7.55, 9.45 |
| 1,000° C. | 0, 0.49, 0.86, 2.0, 3.0, 3.7, 4.75, 5.75, 7.55, 9.2 |
| 990° C. | 9.45 |
| 950° C. | 0, 0.52, 0.92, 2.0, 3.0, 3.7, 4.7, 5.75, 7.55, 9.2, 9.45 |
| 940° C. | 0.52, 0.92, 1.7, 3.0, 3.7, 4.7, 5.75 |
| 927° C. | 2.0, 3.0, 3.7, 4.75, 5.75 |
| 900° C. | 4.7, 5.4, 5.63, 5.9, 6.35, 7.55, 7.75, 7.90 |

Typical structures of the alloys in the beta field showing the Widmanstatten structure are given in figures 8, 9, 10 and 13. In these, the beta decomposed on quenching but it is quite apparent that the alloys were single phase beta solid solution at the quenching temperature. Undecomposed beta is shown in figures 14 and 15. These structures are typical of alloys containing more than 5 percent nickel and quenched from the beta field.

Structures representative of the alpha-beta field are given in figure 11 and 12. These are the microstructures of the 0.52 and 1.7 percent nickel alloys, respectively. It is readily seen that both of these alloys were two-phase at temperature despite the fact that they have been treated at temperatures well above the transformation point of pure titanium. If only a simple binary system were involved with these alloys, they should be beta solid-solution alloys, or increasing nickel content should bring about increasing amounts of alpha rather than the beta phase. However, comparison of figures 11, 12, and 13 shows increasing amounts of the beta phase. Other alloys as shown in figure 1 bear out the same trend, indicating that while nickel itself is lowering the transformation point, some other component is influencing the structure. As pointed out above, it is believed that the basic oxygen content of the titanium is a very significant factor, and the structures of the alloys have been interpreted accordingly. The alpha-beta field indicated in figure 1 is therefore shown as terminating on the zero percent nickel line, in part, at temperatures above the alpha-beta transformation. It will also be noted that the alpha field is not indicated as extending to 875° C. or above as a true ternary alloy would require. The construction adopted in the diagram has been chosen to agree with the data obtained rather than the phase-rule requirements for a three-component system. It is understood that this construction would not be strictly correct if the alloys were true ternary alloys and that conventionally the alpha field should be indicated at some temperature above 875° C. if only titanium, nickel, and oxygen were involved. Since the titanium itself begins to transform below this, it is suggested that impurities other than oxygen (probably iron is quite important) have also influenced the transformation temperature. Iron is present in the titanium and preliminary studies have shown it to behave much like nickel in lowering the transformation.

The composition of the various alloys which have been found to show the alpha-beta structures at the temperature levels examined is given in table 5.

Figure 10. - Microstructure of 1.7 percent Ni alloy water-quenched from 950° C.; showing decomposition product of beta solid solution formed on quenching. X250

Figure 11. - Microstructure of 0.52 percent Ni alloy water-quenched from 900° C.; this alloy is in alpha-beta field at temperature. X250

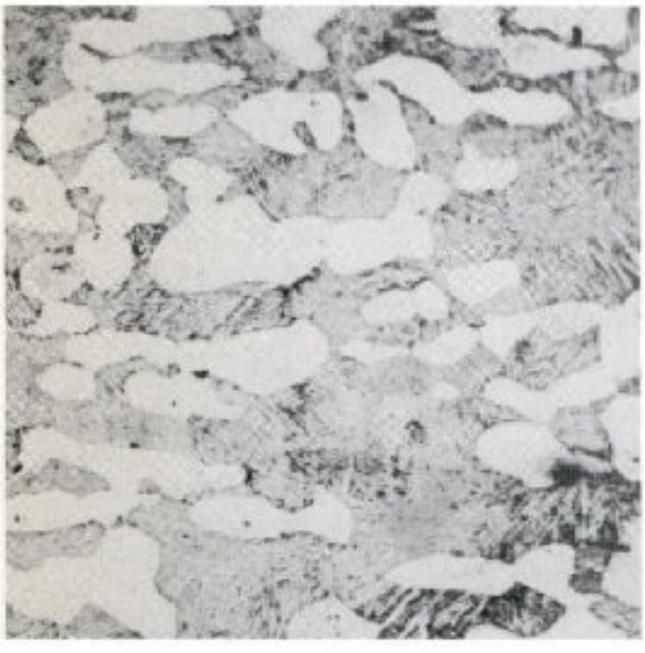

Figure 12. - Microstructure of 1.7 percent Ni alloy water-quenched from 900° C.; this alloy is also in alpha-beta field at temperature. X250

Figure 13. - Microstructure of 4.7 percent Ni alloy water-quenched from 900° C.; alloy is entirely beta solid solution at temperature. X250

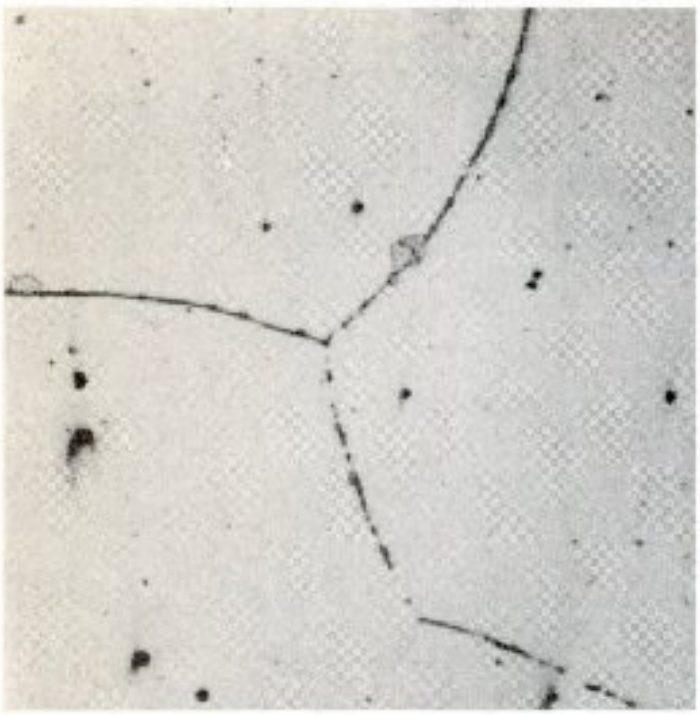

Figure 14. - Beta solid solution in 9.45 percent Ni alloy as quenched from 950° C. X250

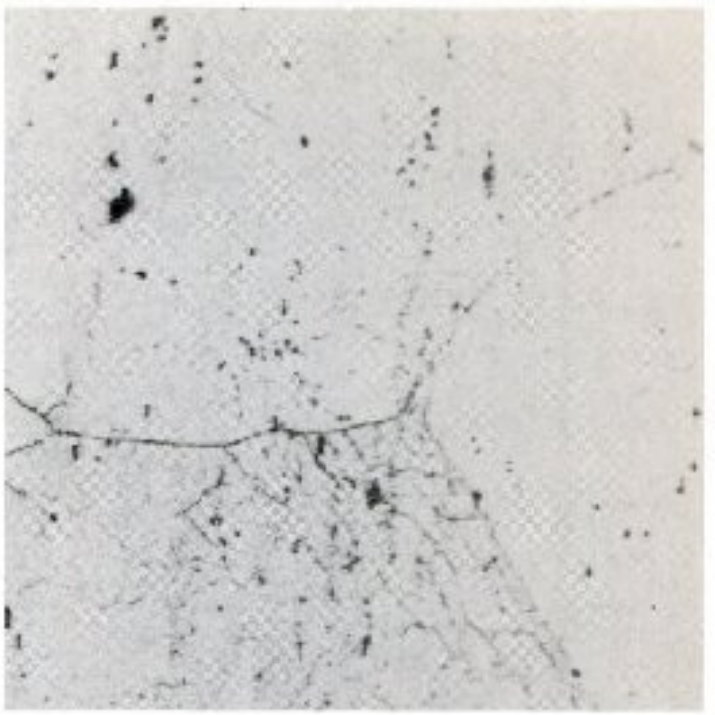

Figure 15. - Beta solid solution in a 7.90 percent Ni alloy as quenched from 900° C. X250

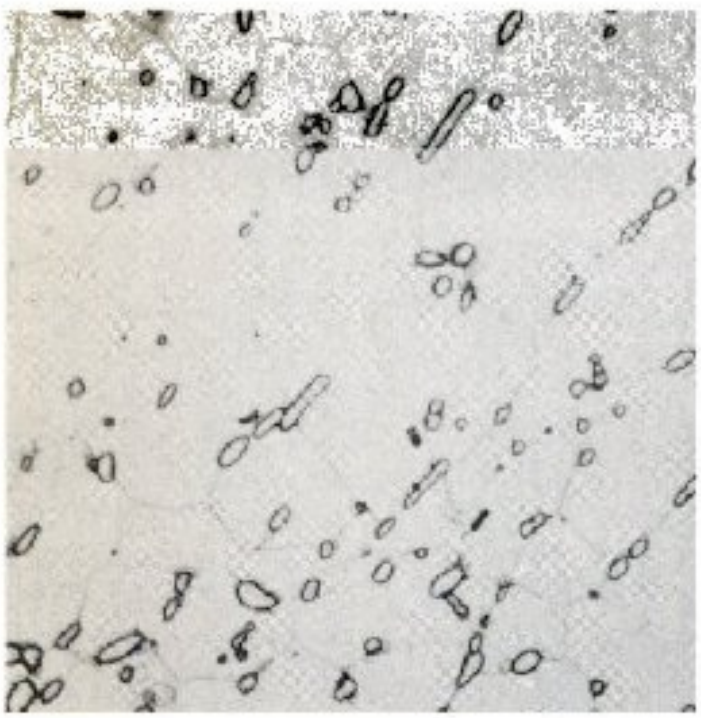

Figure 16. - Beta and gamma in 9.45 percent alloy as quenched from 900° C. X250

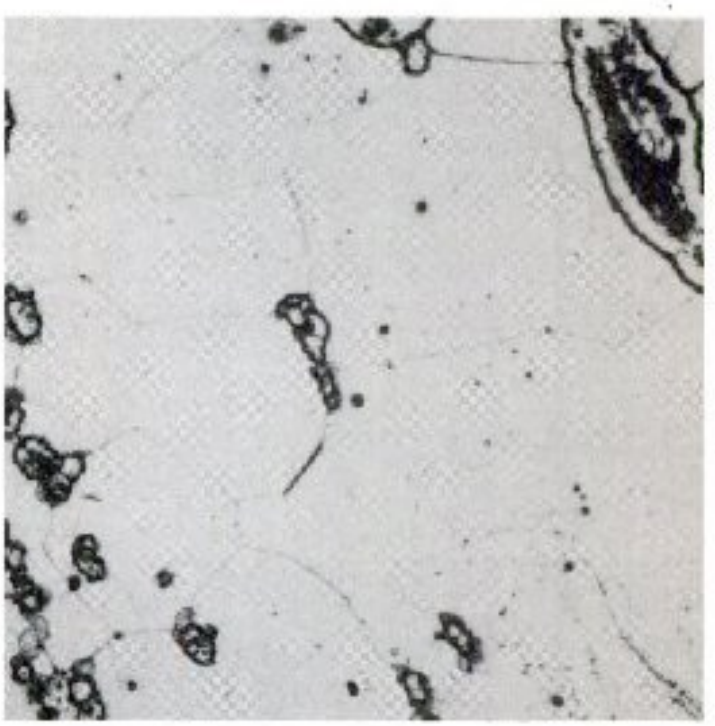

Figure 17. - Beta and gamma in the 14.2 percent Ni alloy quenched from 900° C. X250

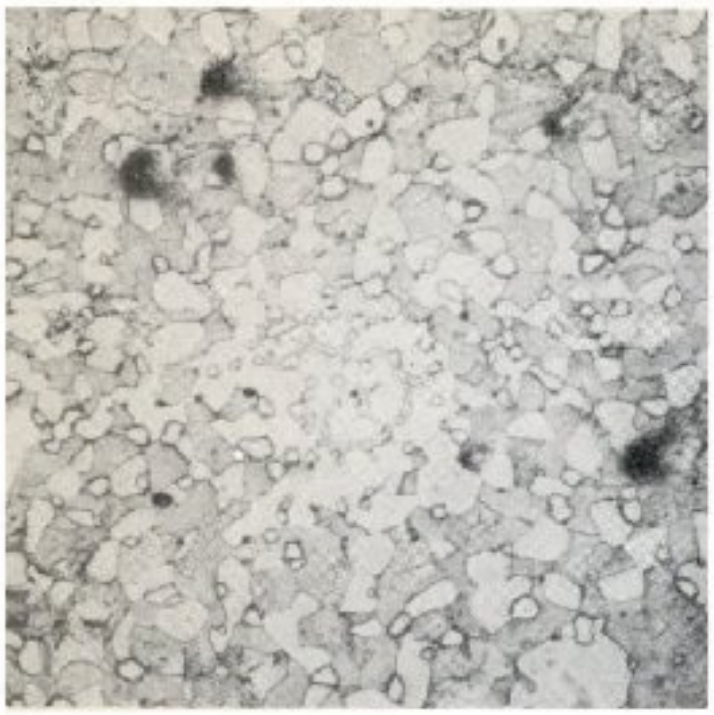

Figure 18. - Three-phase structure of 6.35 percent Ni alloy water-quenched after rolling at 800° C. and soaking 24 hours. X250

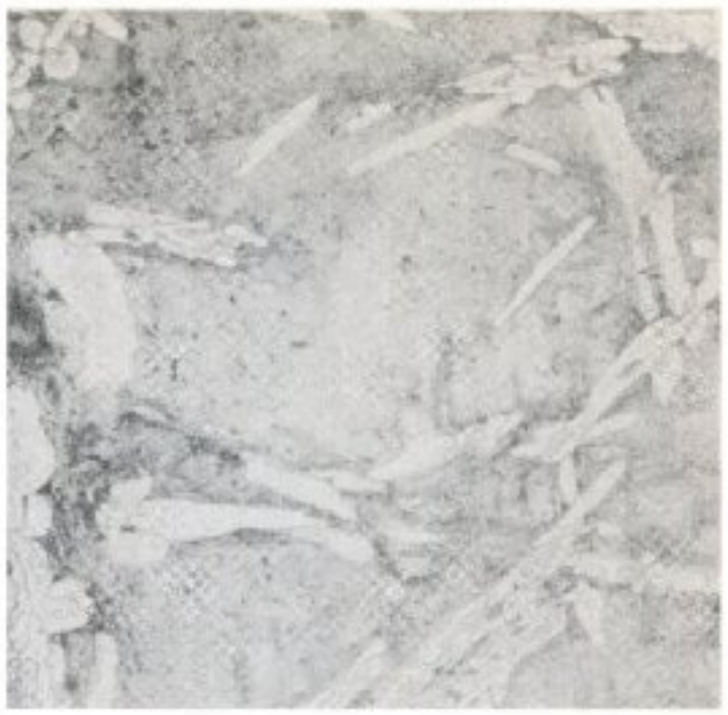

Figure 19. - Three-phase structure in 7.75 percent Ni alloy quenched after heating 18 hours at 980° C. and furnace cooling to and soaking 48 hours at 800° C. X250

Figure 20. - Three-phase structure in 5.9 percent alloy quenched after heating 16 hours at 990° C., furnace cooling to 870° C., and soaking 24 hours at this temperature. Gamma and alpha not distinguishable. X250

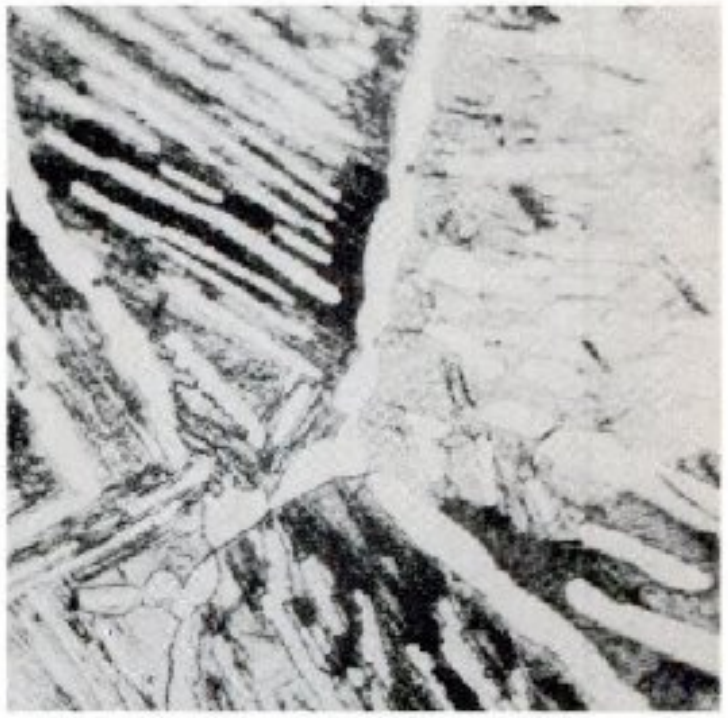

Figure 21. - Three-phase structure in 5.4 percent Ni alloy quenched after 18 hours at 990° C., furnace cooling to 820° C., and soaking 24 hours at this temperature; alpha etched somewhat darker, gamma bright. X250

TABLE 5. - Alloys in alpha-beta field

| Temperature | Composition of alloy |
|---|---|
| 927° C. | 0.0, 0.49, 0.86 |
| 900° C. | 0.0, 0.49, 0.52, 0.86, 0.92 1.70, 2.00, 3.0, 3.7 |
| 870° C. | 0.0, 0.49, 0.86, 2.0, 3.0 |
| 850° C. | 0.0, 0.52, 0.92 |

Figures 16 and 17 are typical of the beta-gamma structures encountered. The 9.45 percent alloy as hot-rolled and quenched from 900° C. is near the beta-gamma boundary and shows small, bright particles of gamma distributed in a background of the beta. Somewhat larger particles of gamma are to be found in the structure of the 14.2 percent alloy, also treated at 900° C. The gamma phase is believed to have a body-centered cubic structure, but there are as yet insufficient data to definitely determine its lattice or parameters. The data on other alloys in the beta-gamma field are given in table 6. This field, as indicated in figure 1, extends beyond 40 percent nickel. The limit of 41.5 percent nickel is assigned on the basis of sharp changes in structure between the 39.8 percent alloy and the 44 percent nickel alloy. X-ray diffraction patterns also show a new constituent in the latter alloy, but brittleness and difficulties with segregation make the present data inadequate to determine whether or not single-phase gamma occurs over a range or as a single composition.

TABLE 6. - Alloys in beta-gamma field

| Temperature | Composition of alloy |
|---|---|
| 950° C. | 9.93, 11.1, 11.5, 13.2, 14.2, 18.4, 23.0, 28.7, 34.4, 39.8 |
| 900° C. | 9.2, 9.45, 9.93, 11.1, 13.2, 14.2, 18.4, 23.0, 28.7, 34.4, 39.8 |
| 870° C. | 8.45, 9.2, 11.1, 13.2, 23.0, 34.4, 39.8 |
| 850° C. | 9.2, 9.45, 9.93, 11.1, 13.2, 14.4, 18.4, 28.7 |
| 830° C. | 11.5 |
| 800° C. | 16.7, 17.4, 18.5, 19.0, 20.7, 28.7 |
| 780° C. | 23.0, 28.7, 34.4, 39.8 |

The structures of alloys treated in the alpha-beta gamma field were easily identified when the gamma occurred as particles closely associated with the alpha, as in figures 18 and 19. Figure 18 (6.35 percent Ni) is typical of the structures developed by hot rolling and holding the alloys at temperatures in which these three phases occur together. The dark constituent is decomposed beta, the lighter constituent is alpha, and the small, bright particles are gamma. Figure 19 (7.75 percent Ni) is typical of structures developed by heating such alloys to relatively high temperatures (980° C.) slowly cooling to temperatures at which the three phase are stable (800° C.), and holding at this temperature. Here it is apparent that on slow cooling both alpha and gamma have separated out of the ground mass and formed in the grain boundary and as well-developed needles. They are, however, readily distinguished from each other. On the other hand, some structures were not so easily identified. Figure 20 (5.9 percent Ni) is also a three-phase structure in which the alpha and gamma particles look very much alike. Heavier etching will nevertheless usually permit differentiation. The alpha constituent is generally attacked more heavily and acquires a darker film while the gamma remains bright. This is illustrated in figure 21. This distinction is fairly easy to make in viewing the structure in the microscope but is not always sharp enough to photograph. Care in etching and visual examination was therefore necessary to outline the alpha-beta-gamma field as indicated.

The compositions of the various alloys showing the three-phase structures at the temperature levels studied are listed in table 7. For the sake of clarity, some of those alloys not important in marking out the field are not included in figure 1.

TABLE 7. - Alloys in alpha-beta-gamma field

| Temperature | Composition of alloy |
|---|---|
| 870° C. | 3.7, 4.75, 5.4, 5.75, 5.9, 6.35, 6.72, 7.2, 7.55, 7.75 |
| 850° C. | 1.7, 2.12, 3.0, 3.5, 3.7, 4.7, 5.4, 5.63, 5.75, 5.9, 6.35, 6.72, 7.2, 7.55, 7.75, 7.9, 9.2, 9.45 |
| 830° C. | 1.82, 2.12, 3.5, 3.82, 5.4, 5.54, 5.63, 5.9, 6.35, 6.75, 7.75, 7.85, 7.9, 9.93 |
| 820° C. | 3.9, 5.4, 5.9, 6.35, 6.75, 7.75, 8.45 |
| 800° C. | 0.52, 0.92, 1.7, 3.0, 3.7, 3.9, 4.7, 4.75, 5.4, 5.75, 5.9, 6.35, 6.75, 7.2, 7.55, 7.75, 8.45, 9.2, 9.45, 11.1, 14.2 |
| 780° C. | 0.49, 0.86, 2.0, 3.0, 3.7, 4.75, 5.75, 6.35, 6.72, 7.2, 7.55, 9.2, 11.1, 13.2, 14.2, 18.4 |

The high-temperature limits of the field have been placed in accordance with the data and to indicate a point contact with the beta field. A line contact could also have been indicated on the basis of the data but that would be suggestive of a four phase equilibrium not justified by the present information. A thin alpha field is shown as the left boundary. This is based on convention rather than the data since no alloys lower than 0.40 percent nickel were examined.

The right boundary of the three-phase field is well-marked through 14 percent nickel in accordance with the data. Beyond this point, however, the small amounts of alpha which might be present were not readily distinguished and the boundary is accordingly dotted to 41.5 percent Ni. The lower boundary of the field is based on the presence of the Widmanstatten structure or undecomposed beta in alloys treated at 780° C. and their absence at 764° C. The distinction is quite definite, since the alloys treated at 764° C. and below show finely divided gamma in a background of alpha.

Typical structures in the alpha-gamma field are given in figures 22 to 25. The 1.7 percent alloy shown in figure 22 was hot-rolled at 900° C., quenched, and rerolled at 750° C., held at this temperature for a short time, and then quenched. The structure developed indicates that at the first rolling, a two-phase alpha-beta structure was developed. On the second rolling, the beta apparently broke up forming particles of gamma in the ground mass of alpha, while the alpha grains were unchanged except for distortion by rolling. Figure 23 shows a similar structure in the 4.7 percent alloy at high magnification. In this picture the small gamma particles are quite plain. Figures 24 and 25 are quite similar structures, both of them were developed by rolling and soaking at 700° C. after previous treatment at high temperatures. The 8.15 percent alloy (fig. 24) shows no large particle of gamma since in its previous treatment it was heated into the beta field while the 17.05 percent

Figure 22. - Alpha-gamma structure in 1.7 percent Ni alloy water-quenched after hot rolling and soaking at 750° C. X250

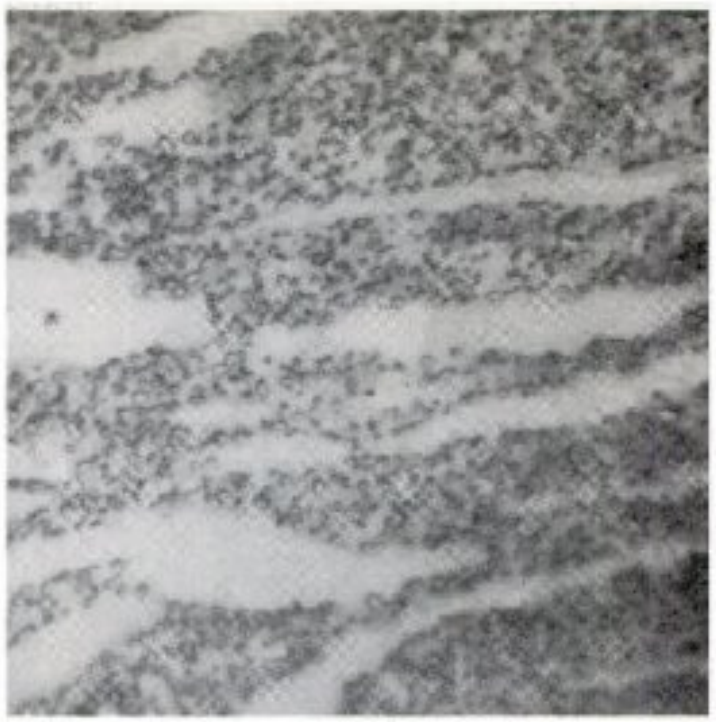

Figure 23. - Alpha-gamma structure in 4.7 percent alloy quenched after hot rolling and soaking at 750° C. X500

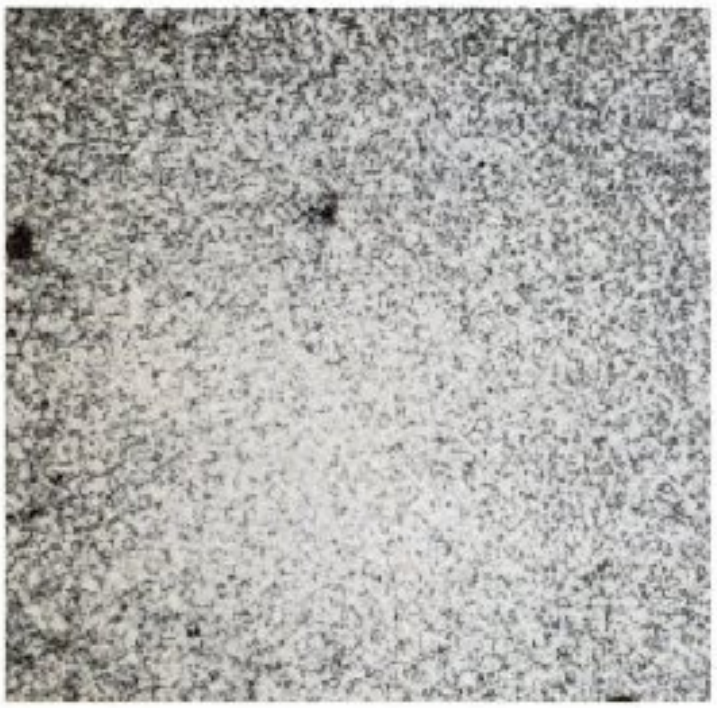

Figure 24. - Alpha-gamma structure of 8.15 percent Ni alloy quenched after hot rolling and soaking at 700° C. X250

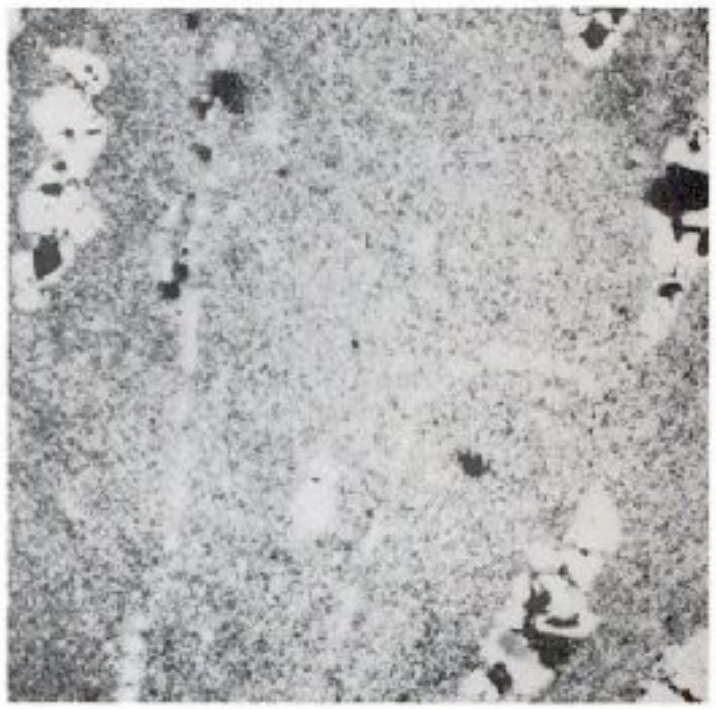

Figure 25. - Alpha-gamma structure in 17.05 percent Ni alloy quenched after hot rolling and soaking at 700° C. X250

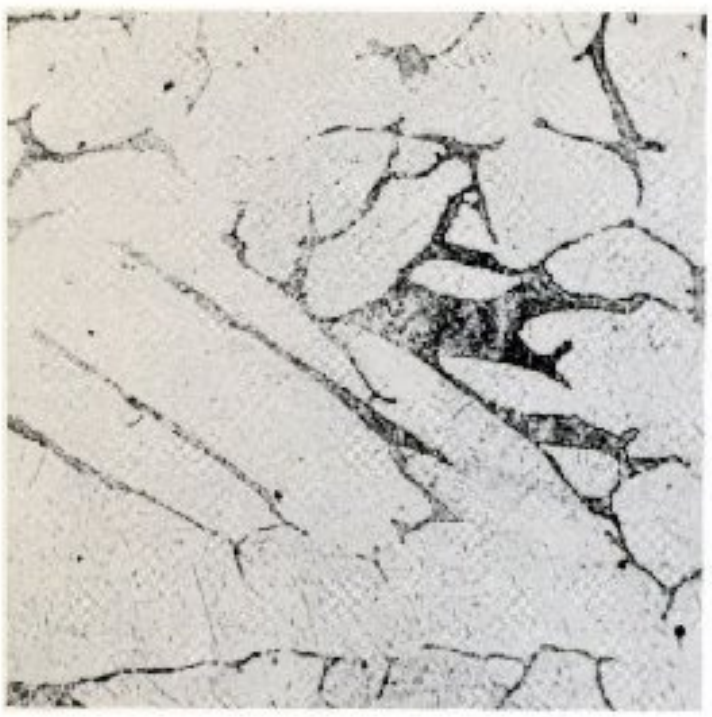

Figure 26. - Alloy of 0.86 percent Ni furnace-cooled after 48 hours at 950° C. X250

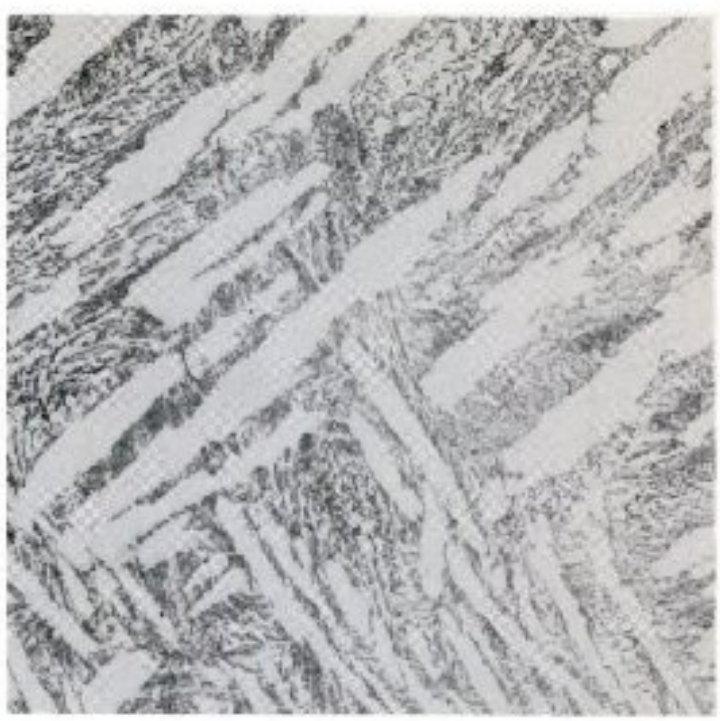

Figure 27. - Eutectoidal structure in 6.75 percent Ni alloy heated 16 hours at 985° C. and furnace-cooled. X250

Figure 28. - Massive alpha and gamma with eutectoid in 7.55 percent Ni alloy furnace-cooled from 950° C. X250

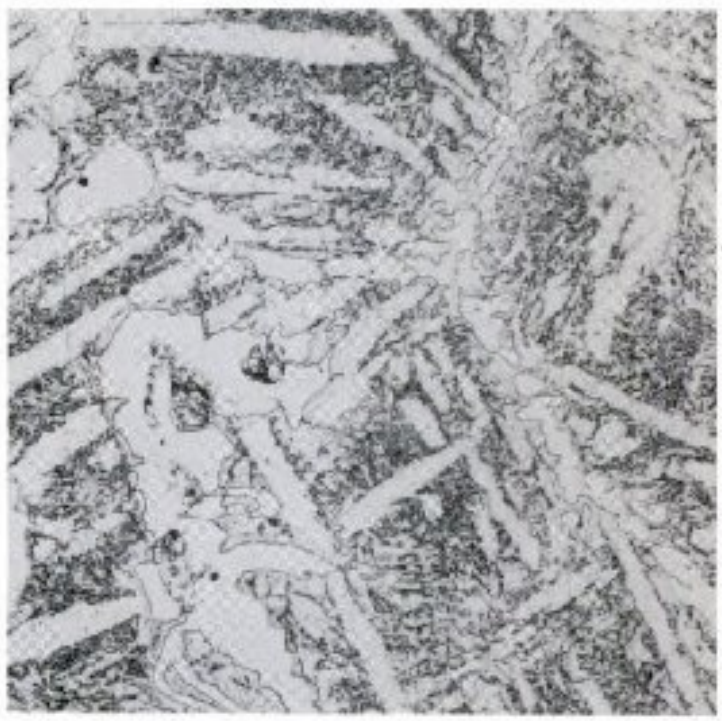

Figure 29. - Furnace-cooled structure of 11.1 percent Ni alloy. X250

alloy was heated in the beta-gamma field prior to the 700° C. treatment. The structures shown in these four pictures are typical of all of the alloys treated at 700 to 764° C. and are indicative of decomposition of the beta to alpha and gamma as shown in figure 1.

Furnace cooling (after 48 hours at 985° or 950° C.) of the alloys did not develop structures useful in determining the phase relationships of the alloys. Structural alterations occurring on slow cooling, particularly through the three phase field, could not be readily interpreted until the diagram of figure 1 had been outlined. They were of interest, however, in that a rather well formed eutectoidal structure was developed. Some of these structures are shown in figures 26 to 29. The 0.86 percent nickel alloy shows a small amount of eutectoid with large amounts of alpha. The 6.75 percent alloy shows larger amounts of eutectoid with alpha needles, while the 7.55 percent alloy shows both alpha and gamma needles with eutectoid. At 11.1 percent nickel, slow cooling from 950° C. developed rather massive gamma along with the eutectoid and some alpha needles.

TABLE 8. - Alloys in alpha-gamma field

| Temperature | Composition of alloy |
|---|---|
| 764° C. | 2.12, 3.5, 5.63, 7.9, 9.93 |
| 750° C. | 0.52, 0.92, 1.7, 4.7, 9.45, 14.2, 18.4, 28.7 |
| 700° C. | 0.4, 0.82, 1.67, 4.35, 5.4, 5.9, 6.35, 6.75, 7.75, 8.15, 8.45, 12.8, 17.0, 23.0, 25.5, 34.4, 39.8 |

These structures suggest that the beta solid solution in the true titanium-nickel binary system decomposes eutectoidally and that the eutectoid will lie between 6.75 and 7.55 percent nickel.

## SUMMARY

The quasi-binary diagram, figure 1, effectively summarizes the data obtained in our study of the phase relationships in the titanium-nickel alloys under investigation. It is quite evident that the impurities present have an important influence on the alloys and that they cannot be considered simple binary alloys but instead behave more like complex ternary alloys. Considerable improvement in the quality of the titanium will be required before high-purity alloys can be supplied on a substantial scale. The investigation of the reduction process in the Bureau's Boulder City laboratories is being continued for the purpose of improving the process, the quality of the metal produced, and the rate of production. These studies and similar efforts in other laboratories will no doubt result in a product of greater purity and hence more satisfactory for large-scale binary alloy work. However, until substantial improvements are realized, the major efforts in alloy studies will have to utilize the present product and the results of such work must be interpreted with due consideration for the limitations imposed by the materials available. This diagram therefore and similar studies on other alloy systems will be of great assistance in evaluating such alloy work.

The effect of nickel on the melting point of titanium is quite marked, amounting to approximately 50° C. for each 1 percent nickel up to approximately 11 percent. At this composition, the melting point is 960° C., and the system appears to have a eutectic at about 33 percent nickel. Nickel is soluble in the high temperature form of titanium showing maximum solubility of 11 percent nickel at 960° C. This solid solution is stable down to 890° C. At lower temperatures it begins to break down forming two- or three-phase structures. One of the new phases that appears is the hexagonal low-temperature form of titanium containing less than 0.5 percent nickel in solution and is designated as the alpha phase. The other phase is a body-centered constituent containing approximately 41 percent nickel and designated as gamma. Decomposition of the beta phase is complete at about 765° C.; below this the alloys consist entirely of alpha and gamma. The diagram suggests that the most useful titanium-nickel alloys may be found in the range of 0.5 to 10 percent nickel. From a consideration of the microstructures obtained, it is evident that such alloys will be amenable to heat treatment and that their properties will likewise be capable of variation over wide ranges. Studies are now under way to determine the physical properties of these alloys in various conditions to determine their fabricating characteristics and the results that may be expected on quenching and tempering treatments.

While the diagram presented is not representative of the pure titanium-nickel binary system, its general features suggest that the true equilibrium diagram will have a rather similar construction. The three-phase field will of course disappear, and the beta phase probably will be found to break up eutectoidally, forming mixtures of the alpha phase doubtless containing less than 1 percent nickel and the gamma phase containing more than 40 percent nickel. The eutectoid temperature has probably been raised by oxygen so that in the binary system it is not likely to be more than 765° C., and since the eutectic horizontal is undoubtedly lowered by oxygen, it will probably not be less than 960° C. A tentative diagram drawn up along these lines is presented in figure 30 as the probable form of the true titanium-nickel system. This diagram of course is not exact. Since the critical temperatures and compositions have been taken directly from figure 1, it should therefore be considered as tentative and applied cautiously until more complete data are available. It is offered at this time in the hope that it will be of assistance in guiding future work on these alloys.

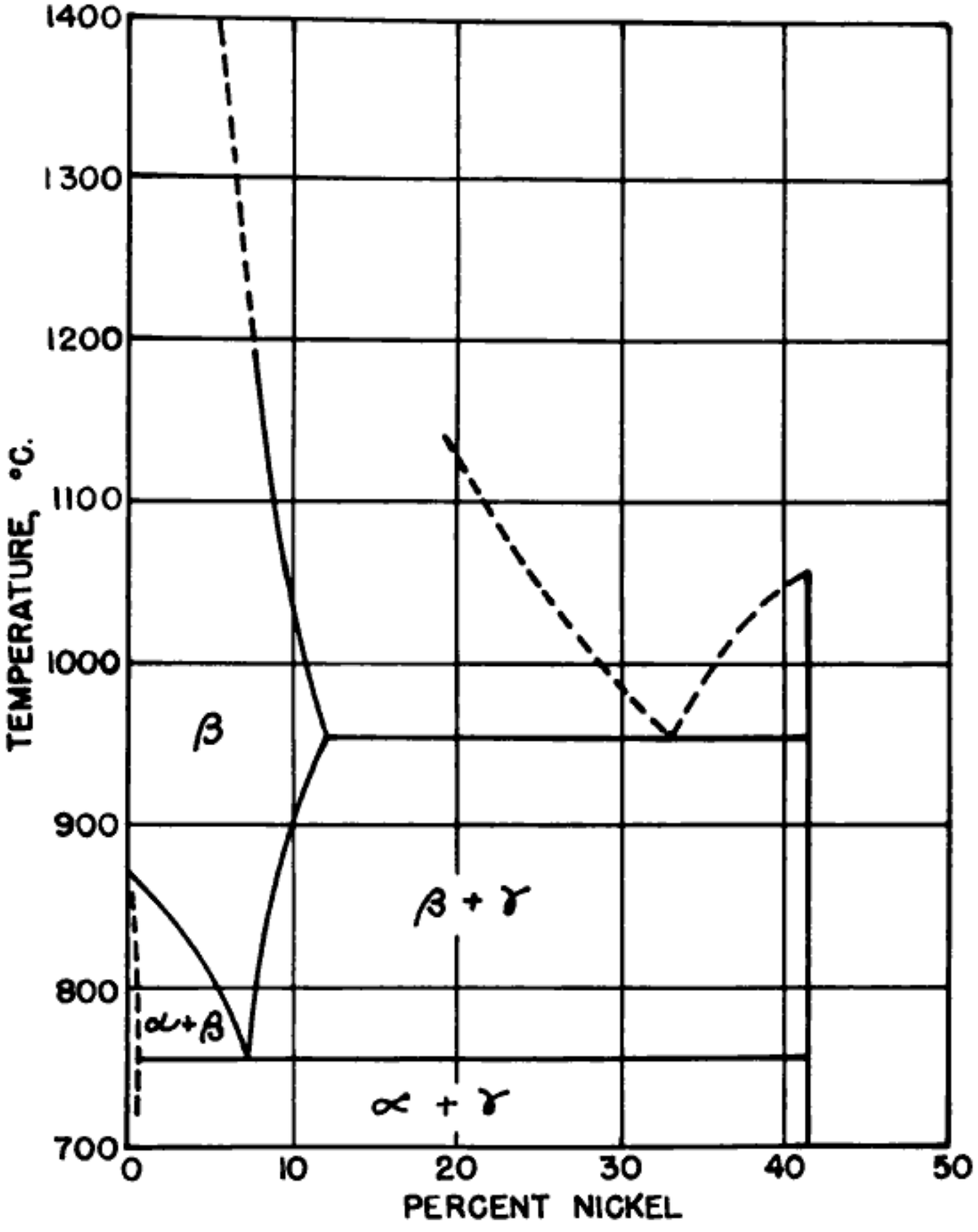


Figure 30. - Tentative equilibrium diagram, titanium-nickel.

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