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PHASE RELATIONSHIPS IN THE COPPER-NIOBIUM ALLOY SYSTEM

M.S. Thesis Submitted to Iowa State University, February 1971

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DIVISION OF RESEARCH UNDER CONTRACT NO. W-7405-eng-82

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Phase relationships in the copper-niobium alloy system

by

Ronald Francis Schelle

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

MASTER OF SCIENCE

Major Subject: Metallurgy

Approved:

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February 1971

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Phase Relationships in the Copper-Niobium Alloy System

Ronald F. Schelle

Abstract

An investigation of the copper-niobium alloy system is reported. Alloys of uniform composition were prepared by remelting arc-melted buttons under an argon atmosphere in a tantalum resistance furnace. No compounds or additional phases, other than a copper-rich and a niobium-rich phase, were observed in these alloys. A transformation was observed at $1085^{\circ}\text{C} \pm 5^{\circ}\text{C}$ which is the fusion temperature of the copper-rich phase. At this temperature the solubility of copper in solid niobium is less than 2.5 wt % and the solubility of niobium in copper is considerably less than 1 wt %. No other transition temperature was observed. In alloys with compositions greater than approximately 70 wt % Cu, a film which appeared to be niobium was observed on the alloy surface. The mechanism by which this film formed is unexplained. No direct evidence of liquid immiscibility was observed in alloys prepared from high-purity, massive metals. A niobium-rich phase, which was spherical and appeared to have been an immiscible molten phase, was observed in alloys prepared from metal powders containing greater than 60 wt % Cu. These metal powders had high oxygen contamination. It appears that if liquid immiscibility does occur in copper-niobium alloys, it must be due to contamination.

INTRODUCTION

Niobium, also known as columbium, is a metal of increasing interest in areas of industrial applications primarily because of its attractive thermal properties, ease of fabrication, and availability of raw materials. Although niobium has been used as an alloying agent in other metals for many years, recent interest in niobium was stimulated by the desire to take advantage of its low absorption cross-section for thermal neutrons and high temperature strength. Applications have been primarily as a fuel cladding and structural material for use in nuclear reactors. Later, this interest has been extended to niobium-base alloys for high-temperature applications in gas turbines, ram jets, airframes and missiles.

Interest in the niobium-copper alloy system has been concerned with the possibility of increasing the corrosion resistance and the mechanical properties of niobium. A major prerequisite for a meaningful study of the properties and behavior of such alloys is an understanding of the phase relationships existing between the component metals as a function of temperature and composition. This report presents the findings of an investigation dealing with phase relationships in copper-niobium alloys and it covers all major alloy regions

between the pure components.

Preparation of homogeneous alloys of two metals, one of which boils at a temperature near the melting point of the other, can present experimental difficulties. Copper, which boils at 2595°C , and niobium, which melts at 2469°C , present such a combination and, therefore, their alloys require some special techniques in preparation and in an investigation of the phase relationships.

Copper, being a metal of antiquity, is well known to most readers, as its use dates to prehistoric times. Familiarity with niobium, however, is considerably less widespread. Thus, a brief summary of the discovery and production of niobium is presented here. Detailed accounts of the early history of niobium can be found in the literature (1,2). The element was discovered in 1801 by C. Hatchett (3) in an ore sent to England more than a century before by John Winthrop the Younger, first Governor of Connecticut. The metal was first prepared in 1864 by Blomstrand (4), who reduced the chloride by heating it in a hydrogen atmosphere. The principal ores of niobium are columbite-tantalite, pyrochlore, and euxenite of which extensive reserves are in Canada, Norway, Africa, and the South America. It is a shiny, white, soft, and ductile

metal and takes on a bluish cast when exposed to air at room temperature for extended periods of time. It begins to oxidize at approximately 200°C in air, and protective atmospheres are thus required for elevated temperature applications. The primary method for commercial production of the metal is the carbon reduction of the pentoxide followed by either consumable-electrode arc-melting or, more recently, by electron-beam melting under high vacuum. Historically, considerable controversy has existed as to whether "niobium" or "columbium" is the proper name for this metal. Presently, both names have wide areas of usage in the literature and in industry.

Niobium metal has a body centered cubic arrangement of atoms while copper has a face centered cubic structure. It is obvious, therefore, that a single phase solid solution can not be continuous between the two components. Furthermore, the extent of any solid solution of one component in the other could be somewhat limited because of the difference in sizes of the copper and niobium atoms. However, only laboratory experiments can yield results on which the true phase relationships can be properly ascertained.

LITERATURE SURVEY

Previous investigations of this system have been quite limited. Elliot (5) studied the occurrence of Laves-phase compounds in various metal systems. He prepared an alloy corresponding to the NbCu_2 composition by arc-melting. X-ray diffraction patterns obtained on filings from this alloy that had been subsequently annealed at 800°C for 10 minutes, indicated a mixture of face-centered cubic copper and body-centered cubic niobium. Metallographic examination of this alloy indicated a segregated structure from which Elliot concluded the system was probably a simple eutectic. A broader survey of the system was made by Argent and Goosey (6). Various alloys were prepared (by arc-melting) from a master alloy containing approximately 58 wt % Nb. X-ray examination of alloys containing 0.3 to 58.5 wt % Nb showed patterns confirming Elliot's findings. By means of metallographic analysis and thermal analysis they constructed a tentative diagram of the copper-rich end of the system. Niobium-rich alloys showed a copper-rich solid solution at the grain boundaries of alloys down to 0.07 wt % Cu in the $709\text{--}1064^\circ\text{C}$ temperature range. They considered the system to be a simple peritectic which they considered as being unusual in metallic systems.

Dwight (7) studied the alloying behavior of niobium by examining arc-melted buttons of niobium alloys by means of metallography and X-ray diffraction. On the basis of his experimental observations and the literature available, forty alloying elements were classified as to whether they formed; (a) solid or liquid immiscibility, (b) continuous solid solution, or (c) compounds with niobium metal. He attempted to melt a button corresponding to the NbCu composition and obtained a round button which contained chunks of copper. He thus classified copper as being immiscible with niobium. No further results or information were indicated.

Popov and Shiryayeva (8) studied the system by means of thermal, metallographic, and X-ray analysis supplemented by physical and mechanical property measurements. The relationships they obtained are shown in Figure 1a. They found a limiting solid solubility of approximately 3 wt % Cu in niobium and only approximately 0.2 wt % Nb in copper. The temperatures of these solubility limits were not given but it is believed that in both cases room temperature was intended to apply. The solubilities were determined by metallographic analysis and microhardness measurements. The diagram reported by these authors indicated a peritectic isotherm at 1100°C

extending from approximately 12 wt % Cu to 99.8 wt % Cu. A region of liquid immiscibility was shown on their diagram; but no evidence was presented in their write-up to support this interpretation of their data. They did, however, observe an invariant temperature at 1550°C , which they took as the monotectic temperature. In reporting this study, Elliot (9), redrew the phase diagram from the thermal analysis data reported and the liquid immiscibility region was eliminated. In the absence of a compound in this system, which Popov and Shiryaeva also confirmed, the 1550°C invariency was unexplainable.

Kieffer and co-workers (10) prepared Nb-Cu alloys by impregnating porous, sintered compacts of niobium powder by immersion in a bath of liquid copper at various temperatures. The physical properties of these compacts were then measured. They concluded that there was a slight, temperature-dependent solubility of copper metal in niobium and a negligible solubility of niobium in copper. The system was suggested as being peritectic in nature and similar to the copper-iron system. The copper-iron system has been shown to exhibit liquid immiscibility only when carbon is present in the iron as a major impurity.

Figure 1. Reported copper-niobium phase diagrams (a) after Popov and Shiryaeva (8), (b) after Allibert and co-workers (11)

In connection with a study of Cu-Nb-W and Cu-Nb-Ta ternary alloys, Allibert and co-workers (11), studied the Cu-Nb system. The relation they obtained is shown in Figure 1b. Thirteen alloys were studied from 1 to 85 at.% Nb content. The only transformation observed in these alloys was a peritectic reaction at $1090^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The thermal analysis was performed using a W-5%Re/W-26%Re thermocouple in a zirconia protection tube. Both the liquidus and the solidus were determined by this technique. On the copper-rich end of the diagram, they adopted the data of Argent and Goosey (6). By means of an electron microprobe analysis, they determined the solubility of copper in niobium at 1090°C as being 2 at.% Cu. X-ray analysis confirmed the lack of compounds in the system. Their thermal data did not indicate an invariency in the region of 1550°C as was reported by Popov and Shiryaeva. They also did not observe any immiscible region, but noted the flat nature of their liquidus promoted a strong tendency for the alloy constituents to segregate on cooling.

MATERIALS, EQUIPMENT, AND EXPERIMENTAL PROCEDURE

Materials

The niobium metal used in this investigation was obtained from the Wah Chang Albany Corporation and was in the form of a 1/2-inch thick slice from a 7 5/8-inch diameter ingot. This metal had a nominal purity of 99.9%, with a Brinell hardness value of approximately 57. The copper used was obtained from the American Smelting and Refining Company. It was in the form of cathode strips, 13" by 3" by 1/4", and had a nominal purity of 99.99%. Table 1 shows the quality of these starting materials as indicated by data supplied by the producers and by qualitative analyses determined by emission spectroscopy at this Laboratory. To facilitate the weighing of portions for preparing alloys, the starting metals were cold-rolled to thicknesses of 8 mils and 16 mils for the copper and the niobium, respectively. Both metals were degreased prior to rolling and the copper was additionally pickled in dilute HNO_3 prior to rolling. Both metals were subsequently degreased to remove any residual oil from the rolling operation. The sheets were then sheared into small pieces for convenience in weighing the components for preparation of the various alloys to be studied.

Table 1. Analysis of starting metals, ppm

Element	Niobium metal value supplied by:		Copper metal value supplied by:	
	Producer	This laboratory ^a	Producer	This laboratory ^a
Al	<20	FTx	NR	--
Ag	NR	NR	NR	T
As	NR	NR	<5	NR
Bi	NR	NR	0.1	NR
C	<30	NR	NR	NR
Fe	<50	FTx	3	--
H	3.7	NR	NR	NR
N	18	(27)	NR	(38)
Ni	<20	FTx	--	--
O	50	(227)	NR	(425)
Pb	NR	NR	7	NR
Sb	NR	NR	2	NR
Si	<20	--	NR	FT
Sn	10	NR	1	NR
Ta	<500	--	NR	--
V	20	NR	NR	--
W	39	NR	NR	NR
Zr	260	--	NR	--

NR = Not reported; -- = Not detected; FT = Faint trace;
T = Trace; x = interference

^aAs determined by emission spectroscopy, except for O and N, which were determined by vacuum fusion.

Preparation of Alloys

Alloys for this investigation were prepared primarily by arc-melting the component metals with a non-consumable tungsten electrode on a water-cooled copper hearth. A helium

atmosphere was used in this operation. The 20 to 25 gram buttons were inverted and remelted four to six times. After this primary melting operation, different methods were employed to further homogenize the samples. High niobium alloys (greater than approximately 80 wt % Nb) were annealed in yttria crucibles at a temperature of approximately 2000°C for 2 hours to produce samples that still retained some non-homogeneity. Some samples were heated to temperatures of 2200 to 2300°C in thoria crucibles where they were predominately, or completely molten depending on the composition. Alloys prepared by this latter method exhibited very good homogeneity. Alloys in the remainder of the composition range (less than approximately 80 wt % Nb) were homogenized by re-melting in yttria crucibles. All of these high temperature homogenizing operations were performed in a tantalum resistance furnace under an argon atmosphere.

Other methods for preparing homogeneous alloys were also investigated. In one method, the arc-melted buttons were cold-rolled into thin sheets which were subsequently sheared into small pieces and arc-melted again. Samples of arc-melted alloys were also placed in a quartz tube which was then sealed under vacuum and heated to a temperature of 1000°C for a

period of twelve days. An attempt was also made to prepare some alloys by a calcium co-reduction of Nb_2O_5 and CuO by a bomb process. The observations on these approaches are described in the Results and Discussion section of this thesis.

Thermal Analysis

In this investigation, a combination of a Pyro-Eye automatic, two-color pyrometer and an optical pyrometer was used to determine the thermal characteristics of the alloy samples. Figure 2 shows an overall view of the equipment used in these experiments. The Pyro-Eye, which was manufactured by the Instrument Corporation of America, was equipped with instrumentation for direct temperature measurement and for output recording. This pyrometer was initially intended to be adequate to determine the thermal characteristics of the alloys during heating and cooling without the necessity of additional temperature measuring devices. It was found, however, that the instrumentation for directly indicating the temperature was not in calibration, and the adjustments provided could not bring the instrument into calibration. It was also found that the response of this instrument varied from one experiment to the next, thus eliminating the possibility of a calibration

Figure 2. Photograph of thermal analysis equipment

- A. Automatic two-color Pyro-Eye
- B. Optical micropyrometer
- C. Beam splitter housing
- D. Tantalum resistance furnace chamber
- E. Control panel for furnace power
- F. Recorder for Pyro-Eye
- G. Power supply for argon purification system

13b

curve from which the true temperatures could be determined. These variations could not be eliminated by several corrective measures which were employed. Experience of other members of the Ames Laboratory indicated this problem was common to this type of instrument.

However, even though the instrument could not be calibrated to indicate the temperature of the sample directly, it functioned quite well to show the relative changes in the sample temperature. Therefore, a system was devised in which the Pyro-Eye was used to measure the relative changes in the color temperature of the sample, and the true temperature was measured independently by means of an optical pyrometer. Figures 3 and 4 show a photograph and a schematic, respectively, of the system employed. A prism-type beam splitter was used so that the Pyro-Eye and the optical pyrometer could be aligned on the sample simultaneously. Using this method, the relative color temperature of the sample could be plotted as a function of time, with discontinuities indicating the presence of phase transformations. Thus, the time-temperature relationship of the sample could be determined without the necessity of contact, which eliminated one possible source of contamination. Also the problems involved with the changing

Figure 3. Photograph of optical equipment employed in thermal analysis

- A. Automatic two-color Pyro-Eye
- B. Beam splitter housing
- C. Optical micropyrometer
- D. Top of furnace chamber

Figure 4. Schematic of sighting arrangement for thermal analysis

calibration of the Pyro-Eye were eliminated.

The optical pyrometer utilized for the true temperature measurement was a Micropyrometer manufactured by the Pyrometer Instrument Corporation. This pyrometer was calibrated against a Leeds and Northrup optical pyrometer that had been calibrated with a National Bureau of Standards tungsten filament lamp. To account for the absorption characteristics of the combination of beam-splitter, sight glass, and any departures from black-body conditions in the system, calibration experiments were performed to determine the melting points of the pure metals, copper, nickel, and iron as well as the allotropic transformations in iron and hafnium. From these experiments, a calibration curve was prepared and used to determine the true temperature from the observed temperature as measured by the optical pyrometer.

The thermal analysis experiments were carried out in a tantalum resistance furnace under an atmosphere of flowing argon. Figure 5 shows the interior of this furnace with the top heat shields removed. The argon atmosphere was purified by passage through Linde type 3A molecular sieves followed by passage through a finely divided copper gauze which was heated to 600°C in a stainless steel tube. The copper gauze was pre-

Figure 5. Photograph of the interior of the furnace chamber, showing the position of the sample within the heating element (top heat shields are removed)

pared by stripping the insulation from a length of stranded 4/0 welding cable and disassembling the cable into its 10 mil diameter wires. The copper was then cleaned by soaking in acetone and washing with a dilute HNO_3 solution, followed by a methanol rinse. The strands were then packed into the stainless steel tube. The atmosphere in the furnace was prepared by evacuating the chamber to approximately 25 microns pressure and back-filling with the purified argon gas. This procedure was performed twice for each experiment. During the heat treating operation, the argon was allowed to flow through the chamber slowly and exhausted through a tube in a filtering flask filled to a depth of 3 inches with Narcoil-40 diffusion pump oil. This oil was chosen for its availability and its low vapor pressure. An empty flask was placed in the line ahead of the oil flask to prevent oil from being drawn into the chamber if reduced pressure occurred during cooling.

In operation, the electric current from a variable power supply was gradually applied by means of a variable-speed, motor-driven speed reducer. After the sample had reached a visible temperature in the furnace, the Pyro-Eye and the optical pyrometer were aligned on a 5/32 inch diameter hole in the tantalum cover on the crucible. The power was then

increased gradually at rates of 5 to 15 °C per minute. The output from the Pyro-Eye was recorded by a Moseley Model 2D X-Y Recorder. Periodic temperature measurements were made and when a thermal break in the plot occurred, the temperature indicated by the optical pyrometer was recorded. The point at which the optical pyrometer reading was taken was noted on the recorder plot by momentarily shorting the input terminals with a normally-open microswitch. This produced a line on the plot to which the corresponding temperature was assigned at the completion of the experiment. The true temperatures of the transformations were then found from the experimentally-determined, calibration curve for the optical pyrometer. For cooling experiments, the motor on the speed reducer was reversed and the cooling proceeded slowly in the same manner as in the heating. The heating and cooling rates were somewhat faster than desired, as there were differences in the arrest temperatures observed on heating and cooling. The rates employed, however, were the slowest attainable with the equipment available. The temperature of the transformation was taken as the average of the initial breaks in the heating and cooling curves. The thermal arrests tended to be less pronounced on heating than on cooling.

Annealing and Quenching

These operations were carried out in the tantalum resistance furnace shown in Figure 6. This furnace has a quenching chamber and is the same furnace used for thermal analysis except that the bottom heat shields have been replaced with heat shields that have a 1 inch tantalum tube through their centers. This tube extends up into the hot zone of the furnace. Figure 7 shows the arrangement employed. The tube acted as a guide to insure that the crucible would drop straight from the hot zone into the quenching fluid directly below. A 2 mil thick tantalum disc that served as a heat shield within the tube was loosely fitted at the bottom of the tube. This disc reduced the amount of direct heat radiation to the quenching oil from the hot zone during the high temperature annealing. Without this disc, considerable vaporization of the oil occurred. The annealing-quenching operation was performed in yttria crucibles under a purified argon atmosphere. The temperature was measured with a Leeds and Northrup optical pyrometer, No. 8636-C, by observing the sample through a 3/16 inch thick Pyrex sight glass.

The crucible containing the sample was placed in a thin-walled tantalum bucket having a bail and support wire of 20

Figure 6. Photograph of furnace for quenching
A. Water-cooled quenching chamber
B. Furnace chamber

Figure 7. Schematic of quenching apparatus

mil tantalum. This support wire was, in turn, hooked to a 5 mil tantalum fuse wire. The arrangement is shown in Figures 7 and 8. The top heat shield which contained the fuse circuit is shown in Figure 9 as well as in Figure 10 where it is located in place in the furnace with the necessary electrical connections.

After an appropriate time at annealing temperature, a current of 10 amperes at 8 volts was run through the 5 mil tantalum fuse. This current rapidly melted this fuse which allowed the bucket with the sample to fall into the quenching bath directly below. When the sample dropped, the 2 mil tantalum disc at the base of the 1 inch tube popped out, allowing the sample to drop into the quenching bath. The quenching fluid employed was DC-704 diffusion pump oil manufactured by the Dow Corning Company. Approximately 1400 ml of fluid was contained in the copper quenching cup, which was water-cooled. DC-704 oil was chosen because it is a single species hydrocarbon and does not contain volatile additives which would evolve during the quenching operation. In actual practice, there was some decomposition of the oil during quenching; the amount depending upon the temperature of the quench.

Low temperature annealing and quenching (1000°C) was per-

Figure 8. Photograph of quenching mechanism
A. Sample bucket
B. Fuse wire
C. Top heat shield

Figure 9. Photograph of the top heat shields showing the 5 mil tantalum fuse wire (arrow)

Figure 10. Photograph of assembled heating unit prior to quenching experiment

formed by placing the samples in a quartz tube which was then evacuated and sealed. The tube was then placed in a muffle furnace and annealed for the desired time. The tube was then removed from the furnace and immediately broken under water to provide a rapid quench. Very little oxidation was observed on the samples during this operation.

Samples that were to be annealed but not quenched were heated in yttria or thoria crucibles which were supported by a tubular tantalum pedestal. The furnace was then cooled at the desired rate after the appropriate annealing time. The thoria crucibles were utilized when the samples were to be annealed at temperatures greater than approximately 2100°C.

Metallography

For metallographic examination, the metal samples were initially sectioned with a standard cut-off wheel with a water stream for cooling the sample. A sectioned piece of each sample was then mounted in "Quickmount" self-setting resin and ground on successively finer grades of silicon carbide discs with No. 600 grit being the final grade employed in this grinding operation. Most of the samples then received final polishing by either of three methods.

The majority of the samples were hand polished by standard procedures using Linde A abrasive and water, followed by final polishing with Linde B abrasive and water. These polishing operations were performed on Microcloth polishing wheels. The alternate method consisted of polishing overnight on a wax wheel mounted in a "Syntron" vibratory polisher with an abrasive of Linde A suspended in water. The sample was then given a final polish, for two hours, on a Microcloth wheel in a Syntron polisher using Linde B abrasive suspended in water. A few of the samples were electropolished with the sample, as the anode, immersed in an electrolyte of 2% H_2SO_4 in methanol. The choice of polishing methods was somewhat arbitrary.

The etchant utilized to enhance the niobium-rich phases consisted of 50 parts H_2O , 10 parts HF , 5 parts HNO_3 , and 5 parts H_2SO_4 . The samples were etched by immersion in the etchant for approximately 20 seconds, then rinsed in water followed by methanol. For etching the copper-rich phases a standard etching solution for copper and its alloys, Gerrard's No. 1 etchant was used. The samples were immersed in this etchant for 5 seconds, then rinsed with water and methanol as for the niobium above. No etchant was required for the elec-

tropolished samples.

Photomicrographs were prepared by standard photographic exposure and printing techniques, using a Bausch and Lomb metallograph with bright field illumination from a tungsten lamp. Some photographs were taken of samples in the unetched condition using oblique illumination.

X-Ray Diffraction

As the alloys in this system were too ductile to allow preparation of powder samples by crushing, samples were taken by means of filing with a steel file. After passing a magnet over the samples to remove any iron filings that may be present, the samples were placed in small niobium-foil packets. These packets were annealed at 800°C for ten minutes to relieve the stresses introduced by filing. A powder sample was then affixed to a thin glass fiber by means of Dow Corning vacuum grease. This fiber was then mounted in a 114 mm diameter Debye-Scherrer X-ray camera that employed Straumanis-type film placement. The sample was then exposed to copper- K_{α} radiation for a period of approximately 6 hours.

The copper and niobium lattice parameters were determined from the data calculated from the resulting film by a least-

squares analysis using a Nelson-Riley extrapolation over the entire angle range. By using the entire angle range, more values were available for determining the lattice parameter of the minor phase present in the high-niobium, and high-copper alloys.

A few qualitative diffractometer scans were performed to verify the crystal structure of quenched alloys. For these survey experiments, a Norelco diffractometer with a logarithmic output was utilized with copper K_{α} radiation. The 2θ angle range was scanned at a rate of 1° per minute from 25° to 140° . Samples employed were solid and had been mounted and polished for metallographic examination previously. This provided a flat surface for scanning. As these were only qualitative surveys, only the diffraction peak locations were analyzed.

Crucible Preparation

For this investigation, a crucible material had to be chosen that would be inert with respect to copper and niobium. It also was required to be stable at temperatures above 2000°C . Refractory metal crucibles could satisfy the temperature requirement, but were unsuitable because of the high solubilities for niobium, which would lead to alloy contamination.

Graphite was also unsuitable as a crucible material, as the niobium would react with the carbon to form a niobium carbide. Refractory materials, such as carbides and nitrides, are, for the most part, more reactive than refractory oxides and pose difficulties in handling and crucible preparation. Of the refractory metal oxides, calcia hydrolyzes in air, magnesia has a high vapor pressure, and zirconia and hafnia, unless stabilized, both exhibit allotropic transformations. These properties cause problems in preparing and using crucibles from these oxides.

Yttria is a very stable oxide up to approximately 2200°C . It is relatively easy to fabricate into crucibles and was on hand for use in this investigation. Consequently, it was utilized for the majority of the crucibles employed in this investigation. Thoria crucibles were prepared for experiments carried out above 2200°C to obtain maximum stability and reduce possible contamination.

Crucibles for use in this investigation were prepared by jolt-packing, and by slip-casting the refractory metal oxides. The jolt-packed crucibles were made by use of a graphite mold and mandrel. The base for the crucible was first formed by packing some refractory oxide on the bottom of the mold. The

mandrel was then inserted and powder packed around it by tapping the mold on a table. When the annular space around the mandrel was completely filled with the refractory, the mandrel was gently removed. The mold with the powder compact was then induction heated under vacuum to sinter the refractory in the shape of a crucible. Both yttria and thoria crucibles were prepared by this method.

The yttria was ball-milled and screened through a 150 mesh screen in preparation for packing. Compacts prepared with this material were sintered at temperatures of 1800-1850 °C for 2 hours in a graphite susceptor. This sintering operation resulted in solid crucibles which were contaminated with carbon. To remove this carbon, the crucibles were heated in air in a muffle furnace for 10 to 12 hours at 800°C. The majority of the crucibles prepared were approximately 3/4 inch in diameter by 7/8 inch in height with an 1/8 inch wall thickness. Some smaller crucibles were also prepared by this method.

A few thoria crucibles were also made by this process. This material was screened to minus 150 mesh which gave a satisfactory powder for jolt-packing. The powder was packed in the graphite mold in a manner similar to that for the yttria,

but the sintering was performed in two stages. The first stage consisted of heating the powder compact in its mold to a temperature of approximately 1900°C for 3 hours under vacuum. This operation yielded a semi-sintered compact that could be handled but was not very strong. Heating the compact/mold combination to a higher temperature would result in considerable carbide formation which, when oxidized in air, would react to form a loose oxide powder. The compact was, therefore, removed from the mold after the first heating and reheated by radiation in the graphite susceptor to temperatures of 2250 to 2300°C for 3 hours. This additional sintering yielded a crucible that was more dense and had satisfactory strength. However, these thoria crucibles were not as strong as the yttria crucibles and higher temperatures would probably be required to obtain crucibles of higher density and strength. The 2300°C temperature reached in the secondary sintering was the upper limit for the induction heating arrangement employed. Graphite wool was wrapped around the susceptor to insulate it, and protect the quartz tube in which the heating was performed. The thoria crucibles were also heated in air to remove any carbon present. During the high temperature annealing experiments subsequently performed with

these crucibles in the tantalum resistance furnace, some additional sintering was evident in the yttria crucibles and to a lesser extent in the thoria crucibles.

Yttria slip-cast crucibles were prepared by Mr. Wayne Calderwood of the Ceramic Engineering Division of the Ames Laboratory. A slip was prepared using reprecipitated yttria. This slip was poured into a plaster-of-Paris mold and allowed to stand until the correct wall thickness was built up. The slip was then poured out and the mold left in air to partially dry. After gentle removal from the mold, the wet crucible was placed in a pallet to dry. The very fragile compact was then pre-sintered on this pallet at 1200°C in a globar furnace. The compacts could then be handled sufficiently to allow placement in a vacuum resistance (tantalum) furnace where they were fired at temperatures of 1850 to 1900°C . The resultant crucibles were tapered and approximately $5/8$ inch in diameter at the base and $3/4$ inch in height. The crucible's wall thicknesses varied and ranged from $1/32$ to $1/16$ inch.

Figure 11 shows a photo of the crucibles prepared by jolt-packing and by slip casting.

Figure 11. Photograph of yttria crucibles prepared for this investigation
A. Jolt-packed crucible
B. Slip-cast crucible

RESULTS AND DISCUSSION

Initial investigations of the copper-niobium alloys system indicated an absence of compound formation and a limited amount of solid solubility between the component metals. Early exploratory investigations indicated that the experimental determination of the system should be relatively straightforward. However, recent, more detailed investigations of this system, while agreeing on the existence of a peritectic horizontal in the neighborhood of the melting point of copper, disagreed considerably on the appearance of the diagram above this temperature; see Figure 1. Allibert and coworkers (11), on the basis of their observations, could not support the existence of either a liquid immiscibility or a 1550°C invariancy as reported earlier by Popov and Shiryaeva (8). Although their investigation did not show either of these features, Allibert and coworkers did suggest the possibility of contamination causing the immiscibility. However, they presented no evidence to verify this interpretation.

There are major difficulties encountered in the investigation of this alloy system. The first problem is in the preparation of alloys of copper and niobium that are both homogeneous and free from contamination. The presence of a liquid

phase in the temperature range of interest in this investigation (above 1085°C) has caused problems of reaction with equipment for measuring thermal properties, such as thermocouples, probes, crucibles, etc. These and other problems have caused the investigation of this system to be anything but straightforward.

Alloy Preparation

In the preparation of most alloys of niobium, arc-melting is the most common method of fusing the components. This is due to the high temperature required to melt the niobium (2468°C). This high temperature causes many container problems as most refractory materials are, at least somewhat, reactive at this temperature. The water-cooled copper hearth used as a container in arc-melting provides very little contamination. Arc-melting of niobium metal is easily accomplished without contamination.

The introduction of copper as an alloying element in niobium complicates the arc-melting process, because it melts at a temperature 1385°C below the melting point of niobium. Thus, when the arc is initiated, the copper melts and has a tendency to run away from the solid niobium before the latter melts. The time involved is very short, which prevents

significant diffusion of the copper into the niobium. If the time is increased or the input power to the arc is increased, a second difficulty occurs, namely the rapid distillation of copper due to its high vapor pressure. This distillation disturbs equilibration of the alloy and also makes it difficult to accurately know the composition of the final alloy button. As the amount of copper for an alloy is increased, the tendency for the molten copper to segregate from the solid niobium during arc-melting increases. Also, the heat conductivity of the alloy is increased with higher copper contents. This allows heat to be removed to the copper hearth at a faster rate which lowers the final temperature of the molten alloy. This causes a smaller portion of the alloy to be liquid at one time. Increasing the power to the arc, in addition to causing considerable copper vaporization, increases the possibility of damaging, or reaction with, the copper hearth.

In anticipation of the above mentioned difficulties in arc-melting alloys for this investigation, other methods of alloy preparation were explored.

A few exploratory attempts were made in preparing alloys by a co-reduction of Nb_2O_5 and CuO using an excess of calcium metal as the reductant. Here, the prospect of having the

constituents evenly distributed prior to alloy formation was the appealing feature. Also, as the reaction was performed in a closed bomb, evaporation of the copper would be held to a minimum. After furnace-firing, it was found that poor slag/metal separation had occurred and considerable metal remained finely divided in the slag. Sulfur was added as a booster; but considerable metal still remained in the slag. While the metal that agglomerated at the bottom of the vessel had fairly good homogeneity, it was felt oxygen contamination must be present. Calcium contamination was also possible, even though it is reported in the literature that there is very little solubility of calcium in either niobium or copper. Since further refining, such as vacuum melting, would remove copper as well as the contamination, the as-reduced metal was considered unsuitable for the purposes of this investigation.

Attempts were made to prepare alloys by sintering mixtures of niobium and copper powders. This process would be advantageous in that the components would be evenly distributed prior to alloy formation. Also, during the sintering operation, adequate time for inter-diffusion of the components would be available; this would permit reduction of the temperature for alloy formation. The powdered metals were thoroughly

mixed, pressed into bars, and sintered at a temperature of 1350°C for 1 hr to determine the applicability of this method. At the temperature employed, the copper was molten and filled the pores between the niobium particles. Metallographic examination indicated very little diffusion had occurred between the components and considerable contamination was present. Since both components, in the powder form, have high affinities for oxygen, it was believed an oxide on the surface of the niobium particles acted as a diffusion barrier.

As sintering did not appear to yield very good results, a series of alloys, in 10 wt % intervals spanning the composition range, were prepared by arc-melting pressed bars made from the powdered niobium and copper. Metallographic examination showed segregation in the resulting buttons. The structures obtained consisted of two phases, one being copper-rich and the other being niobium-rich. In alloys with approximately 60 wt % to 90 wt % Cu, a structure was observed which was interpreted as indicating the presence of liquid immiscibility. In addition to the dendritic structures present, the niobium-rich phase had formed globules which were almost perfectly spherical. These globules were characterized by a band of niobium on the perimeter and a eutectic-appearing mixture

of niobium and copper in the center. Due to their spherical nature and the internal structure present, it is not believed these globules were unmelted niobium particles from the original powder. Figure 12 shows photomicrographs of a sintered sample, to show the original particle shape and size of the niobium powder, and an arc-melted sample that contains the spherical structures discussed above. In subsequent alloys prepared from higher purity, massive starting metals, these spherical structures were not observed. It was concluded that these structures were caused by impurities present in the metal powder, such as possibly oxygen.

It was felt that the high oxygen content and other contamination of the powdered starting metals would always be a problem even if higher purity powders could be obtained. Work with the powdered starting materials was abandoned in favor of massive metals.

Therefore, since it was felt that alloy purity was a major requirement for a meaningful investigation of this system, high purity, massive copper and niobium were obtained and used for this investigation. Arc-melting was chosen as the preliminary method of fusing the massive components of the alloys with as little contamination as possible. This pro-

(a) 70 wt % Cu arc-cast. Niobium in a copper matrix

(b) 75 wt % Cu sintered 1350°C. Niobium in copper matrix

Figure 12. Microstructures of samples prepared from powdered metal mixtures. As polished; oblique illumination; 250X

vided a solid button of the two metals which, if segregation was present, could be further homogenized. After the components were weighed, they were cut into small pieces and arc-melted. The buttons were inverted and melted four to six times. This operation yielded alloy buttons that contained considerable segregation. The segregation increased as the copper content was increased and the resultant buttons were highly irregular in shape due to difficulty in maintaining a molten pool of metal. The temperature obtained in the melting operation was lower with increasing copper content; this prevented the niobium from melting sufficiently to allow rapid dispersion of it into the liquid copper phase. For a homogeneous alloy to be obtained, time would be required for the copper to dissolve the niobium present. The time of the arc-melting operation was too short for this to occur.

The high niobium content alloys, which required the highest temperatures for melting, showed the greatest loss of copper, as noted by the weight loss, due to the melting operation. Chemical analysis of selected alloy buttons substantiated the assumption that the total weight loss in the melting operation was due essentially to copper vaporization, since the compositions by analyses were consistent with the calcu-

lated compositions based on copper being the only component lost during melting.

Homogenization

In efforts to erase the segregation present in the arc-melted buttons, several methods were explored. The first method investigated involved cold-rolling approximately 1/4 inch thick arc-melted buttons into strips of approximately 10 mil thickness. It was observed during this rolling operation that the high niobium content alloys started edge-cracking sooner than the remainder of the alloys. For example, the 90 wt % Nb alloy was only rolled to approximately 18 mils and showed considerable cracking. It appeared somewhat harder than the remainder of the alloys. The 18 mil thickness was the final limit for this alloy without intermediate annealing, whereas the 50 wt % Cu alloy was rolled directly to 10 mils with ease, and could have been reduced further if desired. These thin strips were then cut into very small pieces in a metal shear and arc-melted for a second time. This procedure yielded buttons that were somewhat less segregated than the originally melted buttons, but nonhomogeneity was still present. The slight improvement in homogenization did not appear to justify the considerable time required for rolling,

shearing and remelting the alloys.

Another method attempted was to place portions of the arc-melted buttons in quartz tubes which were then evacuated, sealed and annealed at 1000°C for a period of 12 days. The microstructures before and after this treatment were essentially the same, indicating that very little homogenization had occurred. Other samples (of greater than 50 wt % Nb) were annealed at temperatures up to 1500°C for 4 hours under argon. This treatment reduced the segregation somewhat. However, it was found that high temperature annealing had little effect on samples that contained gross segregation. As long as there was a solid phase present at the annealing temperature, the resulting alloy had some segregation present.

A third method employed was to re-melt the arc-melted samples under argon in either yttria or thoria crucibles in the tantalum resistance furnace. The thoria crucibles were used for remelting alloys of greater than approximately 20 wt % niobium. Thoria was preferred over yttria for the high niobium content alloys because the high temperatures necessary for melting these alloys (approximately 2300°C) required the more inert oxide to prevent contamination. Yttria crucibles were used for the remainder of the alloy compositions. A

sample was heated until it was partially, or completely molten and then held at this temperature for periods ranging from 1/2 to 2 hours, depending on the temperature involved. The shorter times were used at the very high annealing temperatures to keep the copper vaporization at a minimum. Considerable copper was lost during these operations, however. Alloys treated in this manner showed quite good homogeneity. It was found that if the liquid alloy was quenched from the completely molten state, a completely homogeneous alloy with a fine grain structure was produced. This procedure yielded the best alloys as far as homogeneity was concerned.

Metallographic Observations

During the course of this investigation, approximately 200 metallographic samples were prepared and observed. None of these samples, although they had received widely varying heat treatments, showed a completely single phase structure. A second phase was always present in some form or another.

On the niobium-rich end of the composition range, copper was observed at the niobium grain boundaries in annealed samples through 99.4 wt % Nb. This was the highest niobium-content alloy prepared. Attempts to completely dissolve this

copper by annealing were unsuccessful. A sample containing 5.8 wt % Cu was annealed at 1650°C for 2 hours and quenched. Subsequent examination indicated small traces of copper in the grain boundaries. It did not appear that this copper had precipitated during the quench. Samples containing 0.5 to 5.8 wt % Cu were annealed at approximately 1050°C for 3 hours and quenched. This temperature is thought to be near the location of the maximum solubility of copper in niobium. The 0.5 wt % Cu alloy showed copper-rich phase was present in a very small amount, but definitely there. It was uncertain whether this copper had precipitated during quenching.

It is possible that nonhomogeneity present in these alloys caused regions in the sample to have compositions higher than the maximum copper solubility, thus allowing copper to remain after annealing. The mobility of the copper in diffusing through niobium appeared to be very low at these temperatures. Therefore, homogenization by diffusion under these conditions was considered as impractical.

As the copper content of the alloys was increased, the amount of the copper phase present in the microstructure increased proportionally. Figure 13 shows a series of selected photomicrographs that indicate the nature of the solid phases

30 wt % Cu

50 wt % Cu

70 wt % Cu

90 wt % Cu

Figure 13. Photomicrographs showing the nature of the structures present in Cu-Nb alloys. All arc cast then annealed at 1000°C for 12 days and quenched. As polished; oblique illumination; 100X; lighter phase Cu, darker phase Nb

present in this system as a function of composition. These particular samples had been arc cast then annealed at 1000°C for 12 days and quenched. The structures in these alloys were essentially the same as in the arc-cast samples. Some segregation was observed in these samples, but the areas selected for photographing were chosen to represent the structures present in homogeneous alloys of these compositions. As can be seen, there are only two phases present in these samples, the darker niobium phase which shows the arc-cast dendritic pattern and the lighter copper phase.

Figures 14, 15, and 16 are photomicrographs of alloys of 30, 50 and 70 wt % Cu respectively that have been quenched from a high temperature and these same samples subsequently quenched from an intermediate temperature. Figure 16 also includes a microstructure of a furnace cooled 70 wt % alloy. These alloys show the absence of any additional phases being present at intermediate temperatures. A comparison of these figures with Figure 13 shows that the high temperature treatment yields a refined structure with respect to the original arc-cast metal while the intermediate treatment yields an enlarged structure.

As the percent of copper was further increased, niobium

(a) Annealed 2000°C for 1 hr and quenched

(b) Portion of above sample re-annealed 1430°C for 2 hrs and quenched

Figure 14. Microstructures of treated 30 wt % Cu alloy. No additional alloy phase observable. Garrard's No. 1 etch; 100X

(a) Annealed 2000°C for 12 minutes and quenched

(b) Portion of above sample re-annealed 1400°C for 2 hrs. and quenched

Figure 15. Microstructures of treated 50 wt % Cu alloy. No additional alloy phases observable. Garrard's No. 1 etch; 100X

(a) Annealed 2000°C for 30 min. and furnace cooled

(b) Annealed 1670°C for 1 hr and quenched

(c) Portion of (b) re-annealed 1160°C for 8 hrs and quenched

Figure 16. Microstructures of treated 70 wt % Cu alloy. No additional alloy phase observable. (a) Garrard's No. 1 etch; (b) and (c) as polished; oblique illumination; 100X

precipitates could still be observed in alloys through 99 wt % Cu. An alloy of 99 wt % Cu was prepared by heating copper with the appropriate amount of niobium to 2000°C for 2 hours. The niobium present in this alloy appeared to be evenly distributed. This alloy was then annealed at a temperature of 1200°C for 1 hour and quenched. Examination of the quenched alloy indicated a small amount of niobium, in the form of small dendrites, had precipitated on quenching. Other than these small dendrites that came out of solution on quenching, the central portion of the alloys was single phase copper. This treatment should have been above the liquidus as the phase diagram is presently interpreted. However, near the surface of the sample was a globular niobium phase that evidently was present at the annealing temperature. This phase did not seem to show a preference for the top, bottom, or sides of the sample. That this globular structure is related to the previously reported immiscibility is uncertain. If this structure were due to immiscibility, it would be expected that, in order to be so distributed in the microstructure, the solid niobium would have essentially the same density as the liquid copper phase at the annealing temperature. The two-liquid region reported earlier excluded these compositions.

Thermal Behavior of the Alloys

Initial experiments to determine the thermal characteristics of the alloys were performed using a Pt-Pt/13%Rh thermocouple. This thermocouple was protected from direct contact with the sample by an alumina protection tube. In the furnace arrangement employed, the thermocouple cold junction was on the inside of the furnace chamber wall. With the potentiometer corrected for room temperature, thermal analysis experiments performed on pure copper and nickel showed a variation of up to 30°C in the melting and freezing temperatures observed on heating and cooling. The average of these temperatures was lower than the accepted melting point temperature for these metals being tested. For example, the melting point of pure nickel was experimentally determined as 1410°C , while the true melting point is 1450°C . Evidently, the inside thermocouple junction was much hotter than room temperature. This would effectively reduce the overall thermocouple output voltage and thus explain the lower temperature. This was somewhat expected through radiation from the outer heat shield and convection currents in the argon atmosphere in the furnace chamber. It became apparent a calibration curve would be required to determine the true temperature of the sample. This

would introduce further uncertainties and was undesirable, as the cold junction temperature could vary somewhat from one experiment to the next. Furthermore the arrests observed with the thermocouple were not sharp due to the thermal lag through the alumina protection tube.

Although Pt thermocouple, as used above, is stable to about 1700°C , the effective upper temperature for the arrangement employed was approximately 1500°C . This was caused by the close proximity of the heating element to the thermocouple. Experiments run above 1500°C often resulted in the thermocouple wire melting where it passed near the heating element. As it was desired to measure temperatures above 1500°C in this investigation, the possibility of using refractory metal thermocouples, such as tungsten/rhenium, was considered. However, these metals become brittle after heating to a high temperature, and, since the thermocouple had to be removed after each experiment, considerable breakage was very likely. Also, at these high temperatures, the accuracy of these thermocouples is approximately the same as the accuracy of an optical pyrometer. An optical system would have the advantage of not requiring contact with the sample and eliminating the repair steps between experiments.

Because of the experimental difficulties expected in employing thermocouples for the temperatures of interest in the Cu-Nb system, an optical system for measuring temperature was chosen for the thermal analysis.

The optical system devised for thermal analysis, consisting essentially of the micropyrometer, Pyro-Eye, and the beam-splitter, has been described earlier in this thesis. The main problem in the use of this system was the determination of the true temperature of the sample. Three main calibration procedures were explored. The energy absorption characteristics of the beam-splitter and sight-glass combination were determined by sighting on a tungsten filament with, and without, this combination. These observations gave a linear calibration curve and showed the splitter and sight glass absorbed approximately 80% of the light energy. Another procedure employed was to observe the temperature of the sample in the furnace through the splitter/sight-glass combination, and then remove the splitter and sight on the sample through only the sight-glass. The absorption characteristics of the sight glass were known. This also produced a linear calibration curve. The third method was to observe melting temperatures and allotropic transforma-

tion temperatures for various pure metals with the previously described thermal analysis equipment as it was to be used with the copper-niobium alloys. Of the three calibration curves obtained, the second method yielded values that were very close to those obtained by the third method, while the first departed considerably from the other two. This was probably due to departures from black-body conditions present in the furnace. The third method was felt to be more nearly accurate because any departures from black-body conditions would be corrected for, as the sample configuration was the same for all tests. Also the pure metals served as standards which provided a measurable phenomenon that occurred at a definite, known temperature.

The temperature of a thermal arrest was taken as the average of the initial temperatures of the arrests as observed on heating and on cooling. The spread in arrest temperature as determined for heating and for cooling was from 10 to 30°C, and was somewhat dependent on the rate of heating or cooling. The temperature varied slightly during the horizontal arrests and this was due to the changing temperature of the surroundings in the furnace, while the actual sample temperature remained the same.

Transformations observed

The primary transformation observed in alloys of this system on heating and cooling occurred at a temperature of $1085^{\circ}\text{C} \pm 5^{\circ}\text{C}$. It was observed in alloys ranging from 2.5 wt % Cu through 99.0 wt % Cu. It was characterized by an essentially horizontal temperature arrest. This transformation is the fusion point for a copper-rich phase. In view of reports on previous investigations of this system and the fact that this temperature is above the fusion point for pure copper (1083°C), it is believed that this is a peritectic-type transformation. A eutectic transformation would require the temperature to be lower than that for pure copper. As the temperature observed is very close to the melting point of pure copper, and because there is some uncertainty as to the actual temperature, as determined from the calibration curve, one may question whether the transformation temperature is indeed above the fusion point of pure copper. However, the melting point observations for pure copper were, with few exceptions, below this transformation temperature.

Also, metallographic examination of the various cast and annealed alloys obtained in this investigation, showed no indication of a eutectic structure. The majority of the

alloys used for thermal analysis were very slowly cooled. No eutectic was observed in these alloys. Under conditions of faster cooling, a eutectic may appear dendritic in the same manner as a peritectic. With slow cooling, however, the eutectic structure could be present. The only possible eutectic structure observed in this investigation was the internal structure of the globules in the arc-cast alloys prepared from metal powders (see Figure 12). As indicated earlier, the origin of these globules is uncertain, but they are believed to be connected with contamination-induced liquid immiscibility.

The location of the liquidus of this system was difficult to determine. Discontinuities in the heating and cooling curves, which were attributable to the liquidus, were only minor slope changes and difficult to detect. Occasionally these discontinuities also varied somewhat from one heating and cooling cycle to the next for a given sample. On many samples, a discontinuity was not observable either on heating or on cooling. For alloys of greater than approximately 80 wt % Nb, the liquidus was above 2000°C.

At these high temperatures (2000 to 2300°C) the vaporization of the copper from the alloys caused considerable fogging

on the sight glass and made the temperature determination somewhat uncertain. Had the furnace been designed with the gas inlet positioned to direct the argon flow onto the inner surface of the sight glass, this fogging could have been greatly reduced or eliminated. With the equipment employed, a movable disc shielded the sight glass, however, the shield was removed during heating and cooling cycles so the observations could be made. As a result, the sight glass transmission was generally determined at the completion of an experiment in order to obtain a corrected temperature. However, it was sometimes uncertain as to how much fogging occurred after the high temperature measurements were taken.

The location of the liquidus was approximated by visually estimating the fluidity of the sample during annealing experiments, annealing/quenching experiments, and thermal analysis as well as by metallographic examination of the alloys after these treatments. In the annealing experiments, the external shape of the sample after heating to a high temperature gave an indication of the relative amount of liquid present at that temperature. Only a few alloys were quenched from these high temperatures. In these experiments, there was considerable smoking in the chamber during annealing, due to the decomposi-

tion of the quenching oil vapors. This made accurate measurement of these temperatures difficult. However, in these quenching experiments, the presence of a solid phase at the annealing temperature was determined from the microstructures of the quenched alloys. The solid and liquid phase after quenching had marked differences in structure. In the annealing experiments, the sample was cooled at a slower rate which allowed time for diffusion to occur. This made the determination of the presence of a solid phase at temperature more difficult to determine.

With regard to other transformations between the peritectic temperature and the liquidus, no definite trends were found. Popov and Shiryaeva (8) reported a transformation at 1550°C , which they interpreted as a monotectic temperature. Allibert and coworkers did not find this transformation in their investigation of the system. In the initial exploratory portion of the present investigation, melting point determinations were performed on arc-melted samples prepared from metal powders. These experiments were of the Pirani-type in which the temperature of a black-body hole in the sample was measured and the appearance of liquid in the cavity taken as the solidus temperature. At approximately 1115°C , small spots, which appeared brighter than the bulk, were observed on the

surface of the sample, but no liquid was yet observed in the black-body cavity. This phenomenon was assumed to be due to the previously reported peritectic reaction, with the spots being the appearance of the liquid copper phase on the surface. However, at the completion of the experiment, no changes were observable in the sample surface at the location of these spots.

Liquid was observed in the black-body cavity at a definite temperature that ranged from 1450° to 1550°C for alloys in the composition range of 20 to 80 wt % Cu. Later in the investigation, however, thermal analysis experiments on alloys prepared from massive metal did not indicate a definite transformation in this temperature region. The temperatures obtained in the initial exploratory experiments were somewhat uncertain. This 1450° to 1550°C transformation is thought to correspond to the monotectic temperature of 1550°C reported by Popov and Shiryaeva (8). Allibert and co-workers (11) indicated this transformation was possibly connected with contaminants. As alloys prepared from the relatively impure powders initially used in this investigation showed the presence of this transformation and alloys prepared from higher purity, massive metal did not show the transformation, this

explanation is considered feasible, but lacks verification.

Figure 17 is a plot summarizing the transformations and other observations in this investigation. As can be seen, the only transformation repeatedly detected was the fusion point of the copper-rich phase near the melting point of copper. The arrests observed above this temperature were uncertain and scattered. A few samples showed three or four unexplained discontinuities at the higher temperatures.

Other Experimental Observations

X-ray analysis

X-ray diffraction studies in this investigation were limited to powder patterns obtained from annealed alloys which spanned the system, in 10 wt % increments, from 10 wt % Cu to 90 wt % Cu. Diffraction patterns obtained from these samples indicated there were no compounds formed in this system, which agrees with earlier investigations.

The experimental lattice parameter obtained for pure copper was $3.6160\text{\AA} \pm 0.0012\text{\AA}$. This compares with the accepted value for pure copper of $3.6150\text{\AA}$. The values of the copper lattice parameter obtained from alloys up to 80 wt % Nb varied from $3.6082\text{\AA}$ to $3.6212\text{\AA}$. There was a slight trend upward as the copper content was decreased, but it is believed this was

Figure 17. Plot summarizing the transformation data and some other observations in this investigation

caused, in part, by the extrapolation procedures used to obtain the lattice parameter. In the low copper alloys, only a few of the copper reflections were measurable and these were not sharp lines and were in the low-angle region where the Nelson-Riley extrapolation employed is somewhat less reliable. However, it was felt this extrapolation procedure was within the accuracy of measuring the positions of the reflections.

The experimental lattice parameter obtained for pure niobium was $3.2997\text{\AA} \pm 0.0020\text{\AA}$. This compares very favorably with the reported value of $3.3007\text{\AA}$. Niobium lattice parameters obtained for alloys up to 90 wt % Cu ranged from $3.2962\text{\AA}$ to $3.3032\text{\AA}$ with no trends observable.

Since the lattice parameters obtained from the fcc copper and the bcc niobium phases showed no definite variation with composition, the solubility limits for the respective solid solutions are very small.

Qualitative X-ray diffractometer scans were performed on a few quenched alloys to verify the absence of any phase that is stable at high temperatures but decomposes on slower cooling. Table 2 shows the compositions and the treatments given the samples examined with this diffractometer. The diffrac-

tion peaks observed in all of these samples corresponded to the fcc copper and bcc niobium peaks. However, the lattice parameters for these samples were not determined.

Table 2. Compositions and treatments employed on samples examined qualitatively with the diffractometer. All samples were oil-quenched

Sample No.	Composition (wt % Cu)	Treatment
3-149-1	6.4	1650°C for 2 hrs.
3-146-1	27.7	2000°C for 1 hr.
3-145-1	49.7	2000°C for 1 hr.
3-145-2	69.0	1675°C for 1 hr.
3-145-3	68.8	1170°C for 2 hrs.
3-145-4	68.3	1170°C for 8 hrs.

Diffusion couples

Diffusion couples were prepared by two methods. The first method was to clamp the two solid metals together between two steel washers by means of a bolt through the center and tightened with a nut on the bolt. These couples were placed in quartz tubes, evacuated, and annealed at a temperature of 1000°C for a period of 14 days. When the couples were sectioned and examined, there had been considerable diffusion between the bolt and washers, but the interface between the copper and niobium showed no signs of diffusion.

Seven different diffusion couples were prepared by melt-

ing copper around pieces of niobium in yttria crucibles and heating to temperatures ranging from 1100°C to 1740°C at approximately 100°C intervals for a period of 1 hour. The samples were then furnace-cooled from the annealing temperatures. Upon metallographic examination, all of these couples showed that a niobium-rich phase had precipitated out from the copper phase. The amount of this second phase varied from almost nothing in the 1100°C couple to a large amount in the 1740°C couple. Evidently, considerable niobium had dissolved in the copper at the higher temperatures. In the 1740°C couple, the original niobium piece was almost completely dissolved. Although there was considerable precipitation of niobium in the copper phase, there was no copper observed in the niobium piece remaining after annealing. This was somewhat expected as the mobility of the dissolved component would be considerably higher in the liquid copper than in the solid niobium. However, it would be expected that some copper would diffuse in the niobium at 1740°C .

These couples were then analyzed by an electron microprobe. Figures 18, 19, and 20 show microprobe representations of the Cu-Nb interface of the couples annealed at 1100°C , 1320°C , and 1740°C , respectively. These photographs were

(a)

(b)

(c)

Figure 18. Micrographs of the Cu-Nb interface in a diffusion couple annealed at 1100°C for 1 hr. Furnace cooled; 200X
 (a) Beam scanning photograph modulated by sample current.
 Light area is copper; dark area is niobium
 (b) Beam scanning photograph modulated by Nb X-ray intensity
 (in white)
 (c) Beam scanning photograph modulated by Cu X-ray intensity
 (in white)

(a)

(b)

(c)

Figure 19. Micrographs of the Cu-Nb interface in a diffusion couple annealed at 1320°C for 1 hr. Furnace cooled; 200X
 (a) Beam scanning photograph modulated by sample current. Light area is copper; dark area is niobium
 (b) Beam scanning photograph modulated by Cu X-ray intensity (in white)
 (c) Beam scanning photograph modulated by Nb X-ray intensity (in white)

(a)

(b)

(c)

Figure 20. Micrographs of the Cu-Nb interface in a diffusion couple annealed at 1740°C for 1 hr. Furnace cooled; 200X
 (a) Beam scanning photograph modulated by sample current. Light area is copper; dark area is niobium
 (b) Beam scanning photograph modulated by Nb X-ray intensity (in white)
 (c) Beam scanning photograph modulated by Cu X-ray intensity (in white)

taken of the oscilloscope output from the microprobe. The first micrograph, (a) in each figure, shows the variation in sample current of the specimen. This sample current is a function of the atomic number of the elements present. It is an inverse function, in that an element with a low atomic number will yield a high sample current. Thus, copper, which has a lower atomic number than niobium, will yield a high sample current and appear white on the oscilloscope output. The niobium then appears dark.

The second and third micrograph in these figures show the areas of niobium concentration, (b), and of copper concentration, (c), respectively, in the region of the interface. These micrographs are produced by the signal obtained from the spectrometer that collects the X-ray photons that are emitted with the wavelength characteristic of the element desired. The output from the spectrometer then shows the concentration of the specific element corresponding to this wavelength. These concentrations are shown as the white dots in the micrographs. Each white dot, essentially represents one X-ray photon collected by the spectrometer. Electronic-background noise is present, which accounts for some of the white spots between the concentrated areas. Also, it is

commonly observed in diffusion couples, that a small amount of the metal from one side of the interface is smeared onto the other side during the polishing operation.

These micrographs give a semi-quantitative estimate of the composition of the phases present. They show that the niobium-rich phase present in the copper matrix is essentially the same composition as the remaining, original niobium piece. Allowing for electronic noise, the copper phase is indicated as being very low in niobium content.

The composition of the residual niobium piece and that of the dispersed areas of niobium, as well as the composition of the copper matrix, were determined. Scans of the interface were also run to determine if there were any compounds present in the form of thin bands. Only approximate compositions were obtainable from this study even though pure copper and niobium standards were used because the count readings, obtained from the generated X-rays, had to be analyzed manually. This proved to be a formidable task as the volume of data for each sample was large and there were several corrections required to obtain accurate values for the various compositions. A computer program for analyzing the microprobe count readings was only in the preparation stage at the time

of this study. If this program had been available, better composition values could have been obtained.

It was found that there were no intermediate composition bands present at the copper-niobium interface of these couples. However, in the 1100° and 1200°C couples, a thin, discontinuous band of particles in the copper phase was along portions of the residual niobium piece (see Figure 18). The microprobe indicated these particles were of the same composition as the residual niobium. It is possible that this band was part of the original surface on the niobium and contained some contaminant.

The results estimated from the data in the microprobe studies indicated that the copper matrix had not more than 1 wt % niobium dissolved in it, while the residual niobium piece had essentially no copper in it. The dispersed niobium contained approximately 4 to 5 wt % copper. These values were essentially the same for all the couples analyzed.

Niobium-film formation

An interesting and intriguing phenomenon was observed to occur in some of the high-copper alloys. A very thin film of niobium was formed on the surfaces of these alloys. It gave the alloys the appearance of being a silver colored, high nio-

bium alloy, but when the sample was sectioned, the entire center was copper colored. The mechanism by which this film formed is unexplained, but the conditions under which it occurred will be outlined here. Figure 21 shows the cross sectional appearance of this surface film on copper from a diffusion couple experiment at 1450°C . In many alloys where the film was observed, it was not as thick as in this example.

It was first observed on the surface of arc-melted alloys of 80 and greater wt % Cu. In an alloy of 90 wt % copper, the film completely covered all sides of the alloy button. When cross-sections of these samples were examined metallographically, the film was just barely detectable. It appeared to be a layer on the surface to which were attached many small, bead-like areas of niobium in the copper phase. The layer was solid and appeared as though it had been molten.

This layer appeared also on the four lower temperature (1100 to 1420°C) diffusion couples that were prepared. It completely covered the 1100°C couple and was present, but patchy, on the 1420°C couple. When these samples were examined with the microprobe, the film could not be picked up due to its extreme thinness and due to the edge interferences that occurred on scanning off the edge of the sample.

Figure 21. Microstructure at the surface of the copper from a Cu-Nb diffusion couple. Diffusion annealed 1450°C for 1 hr. Indicates Nb film on Cu surface along with Nb globules near this film. Nb precipitates in Cu matrix formed during quench. Garrard's No. 1 etch; 300X

A series of samples was prepared by induction heating copper and niobium pieces in alumina to a temperature of approximately 1225°C for a period of not more than 5 minutes. This heating caused the copper to melt around the niobium pieces. The amount of copper in the charge varied from 90 wt % to 99 wt % of the total. On removal of the samples, it was observed that they all had this coating of niobium on the outer surface. The layer appeared continuous as opposed to a particle conglomeration. It is unknown how this niobium was deposited on this surface when the temperature was considerably below the temperature required to melt such a high niobium content alloy. Also the time at temperature was very short for much diffusion to have occurred. The niobium pieces appeared to be unattacked and in their original form and some of the pieces were only loosely attached to the copper.

When samples were annealed or melted at temperatures above 1500°C in the tantalum resistance furnace, they did not always have the surface film after heating. Some samples that had been completely molten in an yttria crucible showed the film only on the upper surface; the sides and bottom, which were in contact with the yttria, had copper-colored surfaces.

CONCLUSIONS

On the basis of the experimental observations made in this investigation, and keeping in mind the results obtained by previous investigators, the proposed phase diagram for this system has been tentatively constructed as shown in Figure 22.

The transformation at 1085°C is in fair agreement with the transformation reported at 1090°C by Allibert and co-workers (11), and at 1100°C by Popov and Shiryaeva (8). Although previous investigators have proposed that this transformation is peritectic in nature, the solubility of niobium in liquid copper at this temperature is so small that it is difficult to rule out a eutectic on the basis of metallography and thermal data. Experimental results presented here favor the peritectic proposed earlier. However, the very slight increase in the melting point obtained in this investigation, over that of pure copper, is not conclusive evidence of a peritectic reaction.

The solubility limit of copper in niobium at this peritectic temperature is estimated to be not more than 2.5 wt % Cu. Thermal analysis of this alloy indicated an arrest, while alloys with copper contents less than this value did not

Figure 22. Tentative phase diagram constructed from results of this investigation

show an arrest at this temperature. Evidence of a completely single-phase alloy at this temperature and composition was not obtained upon quenching. It is possible that the solid solubility is considerably less than this value. These findings do not support the much greater solid solubility reported by Popov and Shiryaeva, but they are in fair agreement with the estimated solid solubility of copper in niobium at this temperature as reported by Allibert and co-workers. The question of nonhomogeneity present in these alloys, however, adds uncertainties as to the exact location of this solubility limit.

The solubility of niobium in copper at 1085°C is very small (less than 1 wt % Nb). This value is based primarily on metallographic examinations of various annealed and quenched alloys from this temperature-composition region. The melting point of the copper-rich phase being very close to the melting point of pure copper, tends also to support low solubility. The conclusions drawn here, however, are complicated by the presence of the niobium film coating and the niobium globules near the copper surface for some alloys. As indicated, the origin of this film, as well as that of the globules, is as yet unexplained on the basis of present knowledge of this

system. It is felt these niobium structures possibly could form the basis for a proposed liquid immiscibility in this system as reported by some previous investigators. However, in no case in this investigation as well as in all previously reported investigations, has data been presented that definitely substantiates the presence of a liquid immiscibility in any copper-niobium alloys.

The diagram of the copper-niobium system at temperatures above 1085°C is considerably uncertain. The thermal analysis experiments for this region yielded discontinuities that were somewhat reproducible for each alloy sample; however, little relationship existed between alloys. The thermal effects associated with these discontinuities were much less pronounced than those for the 1085°C transformation. Phase boundaries in this region therefore, had to be based largely on other observations. Since no additional phase was observed by various techniques for any part of this region, a valid diagram could contain only a liquidus and solidus.

The presence of nonhomogeneity between the copper-rich, and the niobium-rich phases in these alloys could be the key to many of the uncertainties associated with these upper transformations and solubility limits. This nonhomogeneity problem

proved to be the main obstacle in the investigation of this system, and it was not satisfactorily solved. It is possible, for example, that the multiple discontinuities observed for some of the alloys during thermal analysis could be due to different portions of the sample having different compositions. These different portions could then freeze at different temperatures giving rise to the multiple discontinuities observed. However, metallographic examination of alloys selected for thermal analysis did not indicate the degree of segregation that would be required for the large temperature variation in the discontinuities.

RECOMMENDATIONS FOR FUTURE STUDY

During the course of any experimental investigation, there are, in general, certain aspects of the project that are not fully explained and could use further experimental work. The present investigation is no exception. The following recommendations are made to aid in any future investigations of this system.

1. Some method should be developed to prepare completely homogeneous alloys between copper and niobium. The methods developed and used in this investigation, although they reduced segregation considerably, still left uncertainties especially in the dilute alloys where solubility information was desired. It is felt that powder metallurgy techniques should be the most fruitful; if suitable procedures can be obtained for production and maintenance of contamination-free powders. This in itself, could be the subject of a challenging research project.

2. After a procedure for preparing homogeneous alloys has been developed, a detailed series of quenching experiments should be undertaken on dilute alloys on both ends of the composition range. These quenched alloys should be analyzed by means of metallographic and X-ray diffractometer methods.

This should yield solubility limit information for the regions of solid solution. However, for these experiments, a system must be devised to provide a quench with greater severity than the oil quench employed in this study. Niobium was observed to have precipitated out of solution during the oil quenching operation employed.

3. In connection with these quenching operations, diffusion couples should be equilibrated at various temperatures for extended periods of time, followed by a severe quench. These couples could then be analyzed with the electron microprobe to determine the compositions of the phases present. These experiments are recommended only if a computer program is available to analyze the data obtained from the microprobe. Computer analysis would take into account the complex corrections involved, otherwise only approximate compositions can be obtained, and then only after considerable manual computational effort. The value of the microprobe, when compared with X-ray diffraction and metallographic examinations, is considerably reduced in this type of analysis, when only approximate composition values are obtained.

4. Further examination of the temperature region above the peritectic transformation (1085°) should be performed with

a combination of thermal analysis and metallographic examination of quenched alloys. This temperature region still has considerable uncertainties. It is believed that there are additional, complex reactions occurring at higher temperatures in this system, but the results of this investigation were not conclusive enough to make definite statements in this regard.

ACKNOWLEDGEMENTS

The author would like to take this opportunity to thank Dr. H. A. Wilhelm for the privilege of working under his direction and for the variety of experience gained by being associated with his research group. Also, acknowledgement is given to James McClusky for providing technical and philosophical discussions and suggestions. Recognition is also given to the many personnel of the Ames Laboratory of the A.E.C. who have provided technical assistance and services that greatly aided the performance of this investigation. Special thanks is given to Miss Verna Thompson for her patient suggestions and the preparation of this manuscript.

A very special thank you is extended to my wife, Patricia, for her understanding and moral encouragement provided during the academic and research work involved in pursuing this degree. It is sincerely hoped that this work will aid in providing a better life for her and for my children.

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