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Richard Bruce Loop
(M. S. thesis)

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THE STRUCTURE OF VAPOR DEPOSITED 4D TRANSITION METALS

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ABSTRACT

The structures of electron beam evaporated 4d transition metals, condensed on a helium cooled substrate, were observed using the electron microscope. The samples were annealed to room temperature and removed from the substrate prior to the examination. The elements observed were in the range from zirconium to ruthenium, with the samples consisting of pure elements and various binary alloys.

Evidence is presented that it is possible to form transition metals in the amorphous state, irregardless of composition (i.e., compositions including the pure elements, solid solution alloys, and alloys falling within two phase regions). The stability of the amorphous phase varies with composition, with the least stability occurring for the pure elements, and the greatest occurring for two phase regions. The evidence for bcc elements is more conclusive than that for close packed elements, which present a special case. Amorphous to crystalline transformation temperatures were found to be significantly below values previously reported for 3d transition metals in the case of pure elements. In the center of two phase regions, the transformation temperatures approached $0.3 T_m$, in agreement with values reported for non-transition alloys in two phase regions.

I. INTRODUCTION

M. M. Collver and R. H. Hammond have made a detailed study of the superconducting characteristics and resistance of vapor deposited 4d transition metals.¹ As a result of anomalies observed in the transition temperature of the metals in the as deposited condition, as well as subsequent behavior after annealing, it was determined that an understanding of the as deposited structure would be of value.

Specifically of interest was the possible occurrence of an amorphous structure upon deposition, regardless of whether or not the sample was a pure metal, or what its binary alloy composition was. The interest in the possible appearance of amorphous structures arose as a result of an anomaly in the T_c curve when plotted against the number of electrons per atom, as compared to the normal Matthias solid solution T_c curve.¹⁸

The intent of this work, then, has been to determine within capabilities of the equipment, the structure of the as deposited 4d transition metals, within the range of Zr to Ru. The study is based upon available structural data after annealing to room temperature, in conjunction with resistance data acquired during the anneal from 4° K to room temperature.

The range of compositions observed for each binary alloy system allowed for, in several cases, the stabilization of the as deposited structure (as determined from little or no change in electrical resistance measurements) up to, and above room temperature. This was a necessary requirement before any semi-direct structural observation could

be made of the as deposited structure, due to the lack of in situ electron diffraction capabilities.

Further, an attempt was made to determine, within the working limits of the electron microscope, what the smallest resolvable grain size is for the microcrystalline samples, plus an attempt to establish an upper limit on the possible grain size, or ordered regions, within the amorphous samples, i.e., such that the minimum grain size is known to be of this size or smaller. Alloy systems examined in the study include Nb-Zr, Nb-Mo, Zr-Mo, and Mo-Ru, as well as the pure elements Nb, Zr, and Ru.

A brief review will be made of the conditions under which amorphous metal structures may be obtained, as opposed to non-metals. The production and stabilization of amorphous structures requires a reduction of the mobility of the atom on the surface upon which it is deposited, thus preventing the atom from assuming a position normally required for the stable crystalline structure. This can be accomplished by a number of means, including impurity stabilization, vapor quenching of various types, and co-deposit quenching.

Impurity stabilization requires the presence of a gaseous impurity. For example, a very small partial pressure of oxygen will inhibit the mobility of easily oxidizable material, by most likely covering the deposited clusters with an oxide layer, thus inhibiting further coalescence.

Vapor quenching is achieved by condensing vapor atoms onto a substrate that is sufficiently cold to reduce the atomic mobility (thermal diffusion) and which has a sufficient thermal conductivity to absorb the heat of condensation without undergoing an appreciable rise in temperature. This technique is similar to splat cooling where the sample is

quenched, in the form of small liquid drops, at the rate of $\sim 10^6$ degrees/sec.

Chopra¹⁵ made a distinction between vacuum quenching of pure metal deposits and non-metallic pure materials exhibiting covalent bonding. He reported that pure metals will not form amorphous structures when vapor quenched at helium temperatures.

The distinction was made between the two types of systems on the basis that metals are already close-packed or near close-packed, i.e., similar to the packing for the amorphous structure, whereas covalent materials have very low coordination number (C.N.) when compared to an amorphous structure. Therefore only a very small amount of movement is needed in order to make the structures crystalline in the case of metals. Further, a significant amount of recrystallization is assumed to take place due to higher atomic mobility for metal atoms at reduced temperatures, as a result of higher adsorption and desorption energies.

T. Ichigawa and Fujimi, however, found that while soft, low melting point non-transition metal films do in fact condense (at 4° K) in their stable, or some metastable crystalline structure,⁹ transition metal films, on the other hand, do exhibit an amorphous structure, based on radial distribution studies.¹⁰⁻¹⁴ Fujimi differentiated between the two results on the basis of the electronic structure for transition metals; however, the details of his explanation are as yet incomplete. Results from the present study show agreement with Fujimi for bcc transition metals, while those results for close-packed transition metals are somewhat unclear.

The third method for stabilizing amorphous structures occurs in binary alloy systems, through co-deposit quenching of two elements or compounds which exhibit no solid solubility. The effect of the lack of solid solubility is to create a logjam type of effect, particularly in

cases where the component atoms vary greatly in size, which in turn limits mobility.

Based on work done by Mader et al.⁶ on a number of two-metal systems (in particular Cu-Ag and Co-Au) at 77° K, the following set of conditions were arrived at for the occurrence of amorphous phases: 1.) an equilibrium diagram shows limited terminal solubilities of the two components, 2.) the composition range corresponds to the center portions of the miscibility gap (i.e., allowing for an extension of the solid solubility), 3.) a size difference greater than 10% exists between the incompatible component atoms which do not form solid solutions, and 4.) the substrate surface is amorphous or atomically rough to reduce mobility.

Of further importance to this work is the correlation of a sharp irreversible resistance change with structural changes in a given sample. Two examples of this correlation are given.

The first is one undertaken by S. Mader et al.⁶ in Co-Au and Cu-Ag. In the case of Cu-Ag, the samples were deposited at 77° K, then annealed to room temperature, with the structural examination and further resistance measurements being made above room temperature. He was able to show a direct correlation of a sharp, well defined resistance drop with both an "amorphous" to metastable and metastable to stable crystalline transformation.

A second example is by P. Baier⁴ who performed a detailed study on Pb-Bi alloys, where the sample was deposited at 4° K and in situ electron microscopy undertaken during the anneal to room temperature. In this case several sharp resistance changes were observed, correlating to a number of different phase changes.

II. EXPERIMENTAL

The procedure by which the samples were prepared and T_c measurements made is reviewed here to provide a coherent picture of the means of sample preparation and subsequent structural examination. For a more thorough presentation of these details the reader is referred to masters degree theses by M. M. Collver² and J. A. Roberts.³

A. Evaporation of Samples

The samples were prepared by electron beam evaporation of 4d transition metals onto sapphire substrates in a vacuum of 10^{-7} to 10^{-8} torr. They were removed from the substrate utilizing a method to be described later in this section.

1. Vacuum System and Preparation

The vacuum apparatus consisted of a stainless steel vacuum chamber three feet in diameter by three feet in length, with a liquid helium dewar extending to the center of the chamber from the top. The dewar system consisted of a liquid nitrogen jacket (made of brass), a water cooled plate and 77° K box (made of copper), and a 4° K box made of stainless steel with a copper bottom. The substrate was placed against the copper bottom of the 4° K box during deposition.

The vacuum chamber had three electron gun hearths, one of which was occupied by a rotary gun source used for the deposition of the samples, with a second one being used for the titanium sublimation pump.

The rotary gun consisted of six sources in a rotating crucible, five of which were covered at any given time to prevent contamination.

The pressure in the chamber was brought to the range of $2 - 4 \times 10^{-7}$ torr utilizing a warm water "bake-out" ($\sim 100^\circ \text{C}$), a mechanical roughing pump, and an oil diffusion pump. The base pressure was further reduced to $3 - 6 \times 10^{-8}$ torr by utilizing a liquid nitrogen cooled plate (at the back of the vacuum chamber), plus a titanium sublimation pump. The major impurity, as indicated by a residual gas analyzer, was H_2O .

2. Substrate and Substrate Preparation

The substrate used consisted of sapphire single crystals ($1/16" \times 1/2" \times 1"$) of an orientation which provided optimum thermal conductivity. The substrate was cleaned using a Teepol soap solution, followed by boiling for 30 minutes in a 50-50 $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (distilled) solution, in turn followed by boiling in distilled water. Contacts consisted of two types, gold or silver. The gold contacts were evaporated onto the substrate, while the substrate was held at 300°K (in a vacuum of 10^{-6} torr). When silver contacts were used, they were painted on using a special paint. Gold, as well as indium, was used to provide better thermal contact between the substrate and the 4°K box during deposition.

3. Method of Evaporation

The sample was prepared by placing a metal slug in the water cooled crucible and bombarding with an 8 KV electron beam. The rate of evaporation was controlled by a feedback signal provided by an Allen Jones Electronic evaporation rate monitor. The rate variation was within 5 %. In order to calibrate the rate monitor, times and rates were selected to make films having thicknesses in the range of $1000 \text{ \AA}$.

Thickness measurements were made using a Tolansky multiple interferometer. The rate monitors were then calibrated using these measured thicknesses. To ensure that there was not a significant increase in temperature during deposition due to radiation effects, a superconducting molybdenum sample was exposed to radiation resulting from heating tungsten to a white heat (point of evaporation). The sample did not go normal, thus indicating that the temperature rise during deposition was not significant (below 7.2° K).

4. Evaporation of Alloys

In those cases where an alloy of a certain composition was desired (and where the vapor pressures of the two components were different), the alloys were pre-mixed in a pre-calculated ratio, such that as a result of the different vapor pressures, the desired composition was attained upon deposition. The compositions of the samples were determined using an electron microprobe. In those cases where the samples were less than the optimum thickness (i.e., effectively infinite thickness), the composition determination was based upon calibration curves for the microprobe as per W. E. Sweeney et al.¹⁶

B. Critical Temperature Measurements and Annealing Procedure

1. T_c Measurements

The critical temperature was measured using two point contacts (supplying a constant current, then measuring the voltage across it). Measurements below 4.2° K were made by pumping on the liquid helium - allowing a minimum temperature of 1.7° K to be reached. For temperatures above 4.2° K a low power heater was used, allowing for a temperature rise to approximately 5.5° K. Above 5.5° K the substrate box

itself was allowed to warm up in the absence of helium, at a rate of approximately 0.2 to 0.4° K/min.

2. Annealing of Samples

After the T_c measurements, the samples were annealed at a rate of 1 - 3° K/min. Two different methods were used: 1.) Warm helium or N_2 gas was flowed into the liquid helium dewar, or 2.) The substrate box was bombarded by electrons from a filament located on the liquid nitrogen cooled shield. To prevent possible damage to a Ge thermometer located on the 4° K plate, annealing temperatures were limited to values below room temperature. The sample resistance was determined by sending a constant current of either 1 μA or 10 μA (depending on the sample resistance) through the deposited films, with the resulting voltage drop across the samples being measured with an Astrodata Nanovoltmeter (Model 121 RZ).

C. Electron Microscopy

1. Sample Preparation

The electron microscopic examination of the samples took place after they had been annealed to room temperature and the composition determined using the electron microprobe. Several techniques were tried in order to remove the samples from the substrate, including 1.) mechanically scraping the sample off, 2.) using a LiF substrate, then dissolving the substrate in order to remove the sample, and 3.) using cellulose acetate to lift the sample off the sapphire substrate. The third method (cellulose acetate) gave the most consistent results, and hence will be described in detail.

First, the sample is scribed with a knife or other sharp instrument

to the approximate size desired for the microscope examination, i.e., somewhat smaller than the microscope grid to be used. A strip of cellulose acetate is then partially dissolved, placed over the sample to be removed, and allowed to dry. A second layer of cellulose acetate is then added for strength. Following this, the sample is removed from the substrate by carefully lifting the cellulose acetate, after which the acetate and sample is placed in acetone, with the cellulose acetate being allowed to completely dissolve. It is noted that in several cases the sample broke into pieces smaller than that originally scribed (due most likely to the sample thinness). However, pieces of a sufficient size were still obtainable in all cases.

The samples are then floated onto a microscope grid and placed in a bath of distilled water. The purpose of this step is to remove any folds or wrinkles acquired through the previous steps by utilizing the high surface tension of distilled water. The sample is then refloated onto a microscope grid and either placed in the electron microscope or stored in denatured alcohol until such time as the electron microscopic examination is made. Washing the microscope grid in alcohol before picking up the specimen aids in breaking the surface tension of the distilled water. It is important to ensure that all of the cellulose acetate is removed from the specimen prior to placing it in the electron microscope so that there is nothing to interfere with the thermal contact between the sample and the microscope grid (necessary to ensure a minimal temperature rise during the time the sample is illuminated by the electron beam).

Scraping the film from the substrate in order to prepare the microscopic samples was unsuccessful for the simple reason that the sample was too thin to obtain usable pieces. Use of the LiF introduced

a new variable into the problem, specifically, possible effects that a different structure and material might have on the structure of the deposited film.

2. Sample Observation

The microscope used for the majority of the observations was the Hitachi (Model HU-125). The Hitachi (Model HU-650) was used in a few special cases where the thickness of the sample required it.

The technique employed in the actual observation was to undertake a search of the specimen in the diffraction mode to determine what structure was present, and whether or not the structure was uniform throughout the sample. Following this, both dark and bright field micrographs were taken, the bright field in order to identify the area observed, and the dark field to give an indication of the grain size and size distribution (in those cases where the sample was clearly crystalline). The normal procedure was to take a series of three photographs - Bright Field (B.F.), Dark Field (D.F.), Selected Area Diffraction (S.A.D.) from each given area.

Voltages generally employed were 100 KV, with some instances of 125 KV, allowing greater sample penetration. Magnification ranged from $\sim 15,000$ to $105,000\times$, with the higher value being used to determine what the smallest observable grain was under conditions of optimum resolution, and whether or not any grains were visible in the amorphous samples under the same conditions.

3. High Temperature Observations

The hot stage used for high temperature annealing of those samples which were amorphous at room temperature was a production model by Hitachi. It provided a temperature range up to $\sim 900^{\circ}\text{C}$, and was

provided with a thermocouple, though no means of measuring sample resistance was available (due to the need for good thermal contact between the sample and grid to prevent heating).

The procedure employed in this case was to slowly anneal the sample, while observing it in the electron microscope in the diffraction mode, until such time as the diffraction pattern transformed from an amorphous to a crystalline pattern. Selected area diffraction patterns were made during the course of annealing, and after the sample had been cooled to room temperature, in order to make structural determinations.

III. RESULTS

The particular alloy compositions examined were chosen in order to facilitate the comparison of the measured T_c for thin film samples vapor deposited at 4° K with the normal solid solution bulk T_c curve for the same 4d transition metals. The structures present at room temperature, as determined by electron diffraction, can be separated into two groups - those exhibiting small grained crystalline patterns and those exhibiting diffuse, amorphous appearing patterns.

A. Crystalline Structures

Those systems which exhibited crystalline diffraction rings consisted of pure elements and binary alloys of compositions lying in the solid solution regions of their respective phase diagrams (and extensions of these solid solution regions, which will be discussed in the final section). Samples in this group included binary compositions of Nb-Zr, Nb-Mo, and Mo-Ru, as well as pure niobium, zirconium, and ruthenium. The grain sizes observed ranged, in general, from 10-20 Å to ~2500 Å. The smaller limit was inferred from the presence of continuous, as opposed to spotty, diffraction rings.

This group can be further divided on the basis of resistance measurements taken during the annealing of the samples from 4° K to room temperature. These two subgroups consist of 1.) bcc elements and their near alloys, and 2.) hcp elements and their near alloys. Representative diffraction patterns and resistance -vs- temperature curves are shown in Figs. 1 - 6.

1. bcc Elements and Near Alloys

Samples occurring in this group include compositions falling within the Nb-Zr, Nb-Mo, and Mo-Ru systems, plus pure niobium. These samples all showed a sharp, irreversible drop in sample resistance at some well defined temperature below room temperature. The magnitude of the drop, however, varied fairly widely.

a. Nb-Zr System (Nb rich)

Samples in this system were prepared using a previously prepared solution of Nb and Zr. Sample compositions were varied by burning off varying amounts of zirconium between each sample preparation. This served to decrease the zirconium content in each succeeding sample as the zirconium had a higher vapor pressure. The individual sample compositions were then determined upon removal from the evaporator.

T_c measurements as deposited ranged from 5.4° K to 5.9° K in a linear manner with the increase in niobium content. After annealing past the temperature at which the resistance drop occurred, and remeasuring the critical temperature, it was found that the T_c approached the expected bulk value. The temperature at which the resistance drop took place varied between 90° K and 170° K. Grain size measurements at room temperature using electron microscopy indicated a very fine crystallite size, ranging between an approximate minimum of 70 Å and an approximate maximum of 3000 Å. The data for this system are summarized in Table I.

b. Nb-Mo System (all compositions)

Samples were prepared in this composition range to provide additional data to compare the proposed amorphous T_c curve with the bulk solid solution T_c curve. Evaporated samples were prepared in

a manner similar to that for Nb-Zr. Sample compositions were determined, after annealing to room temperature, using the electron microprobe. The structure for all samples in the system was found to be bcc. T_c measurements at deposition ranged from 5.5° K to 8.2° K, the measured value increasing, in general, with increased Mo content.

All samples showed a sharp resistance drop with one exception, this being Nb_{.30}Mo_{.70}. This exception was felt to be due to a faulty measurement at low temperature. Again, after annealing past the temperature at which the resistance drop occurred, and remeasuring T_c , it was found that the critical temperature approached the expected bulk value. The resistance drops took place between 40° K and 110° K. The minimum resolvable grain size was $\sim 50 \text{ \AA}$, with the maximum observed grain size being $333 \text{ \AA}$. The data for this system are summarized in Table II.

c. Mo-Ru System (Mo-rich)

Samples for this system were prepared in a manner similar to the above two systems. Again, the structure for both samples observed in the electron microscope was bcc. T_c measurements as deposited were 8.9° K and 9.4° K, with the increase corresponding to the increase in ruthenium content. The value at 9.4° K represented the peak value in the amorphous curve. The T_c for both samples was found to approach the bulk value after annealing to room temperature. The temperature at which the resistance drop took place was between approximately 100° K and 300° K, as indicated in Table III. Both samples were fine grained, with the grain size ranging between $50 \text{ \AA}$ and $1000 \text{ \AA}$.

2. hcp Elements and Near Alloys

Two samples occurring in this region were observed by electron microscopy, these samples being pure zirconium and ruthenium. Annealing data only are available on other samples, these consisting of $\text{Mo}_{.10}\text{Ru}_{.90}$ and $\text{Mo}_{.03}\text{Ru}_{.97}$. These are included in that they fall in the solid solution region near pure ruthenium. Further, their annealing curves exhibit similar characteristics to that for pure zirconium and ruthenium. The hcp elements and near alloys were observed to exhibit a gradual resistance change upon annealing, showing either a positive or negative slope. The resistance change during annealing was an irreversible process for all cases. Data are summarized in Table IV.

a. Zirconium

The one sample of pure zirconium observed showed a fine grained polycrystalline pattern, the structure being a super-position of hcp and what is most likely a metastable fcc structure. The T_c measurement as deposited was 3.3°K . After annealing to room temperature, the T_c value was found to decrease toward the expected bulk T_c value.

b. Ruthenium

Pure ruthenium also showed a fine grained crystalline diffraction pattern. The structure was indexed as the stable hcp phase. A minimum resolvable grain size of $35 \text{ \AA} - 40 \text{ \AA}$ was observed. The transition temperature was determined to occur at a value less than 1.7°K both in the as deposited state, and after annealing to room temperature.

c. Mo-Ru System (Ru rich)

The resistance data upon annealing for $\text{Mo}_{.10}\text{Ru}_{.90}$ showed a smooth decrease from 4°K to room temperature. For $\text{Mo}_{.03}\text{Ru}_{.97}$ and pure Ru, the

resistance data showed a continuous positive slope with temperature between 4° K and room temperature. After annealing to room temperature and recooling, the T_c was found to approach the expected bulk values.

B. Amorphous Structures

Those systems exhibiting diffuse, amorphous appearing diffraction patterns consisted of binary alloys which occurred in two phase regions of their respective phase diagrams. Three systems are represented in this group - these being Nb-Zr, Zr-Mo, and Mo-Ru. All samples in this group were prepared in the same manner as previously discussed for the crystalline cases. Further, all samples showed a gradual slope in the resistance-vs-temperature curve. The data are summarized in Table V. A representative diffraction pattern and annealing curve are shown in Figs. 3 and 6.

1. Zr-Mo System

One composition was observed in this alloy system, this being $Zr_{.85}Mo_{.15}$. Electron diffraction revealed a two ring diffuse, amorphous appearing diffraction pattern, with no discernable grain size visible in the dark field mode. During annealing the resistance showed a gradual decrease. The critical temperature upon deposition was 4.1° K. This value remained essentially unchanged after annealing to room temperature and recooling.

2. Nb-Zr System

Two compositions were observed for the Nb-Zr system ($Nb_{.60}Zr_{.40}$ and $Nb_{.67}Zr_{.33}$). Electron diffraction patterns revealed three ring diffuse, amorphous appearing diffraction patterns with no discernable grain size

in the dark field mode. Both samples showed a gradual decrease in resistance upon annealing to room temperature. The measured T_c 's upon deposition were 4.8° K and 4.6° K respectively. After annealing to room temperature, then remeasuring the critical temperature, both samples showed a decrease in T_c , whereas an increase would be expected, if annealing had taken place, due to the fact that the bulk T_c is higher. This change could possibly be the result of the beginning of a transformation to a metastable structure. This possibility is discussed in the next section.

3. Mo-Ru System

Alloy compositions examined in this system consisted of $\text{Mo}_{.68}\text{Ru}_{.32}$ and $\text{Mo}_{.50}\text{Ru}_{.50}$. Electron diffraction patterns again revealed three ring diffuse, amorphous appearing diffraction patterns. Dark field electron microscopy revealed no discernable grain size. Again, both of these samples showed a gradual resistance decrease upon annealing. The critical temperatures upon deposition decreased from 8.8° K to 7.7° K with increased ruthenium content and remained essentially unchanged after annealing to room temperature.

C. Annealing in the Electron Microscope

Three different samples were annealed using the hot stage attachment to the HU-125 microscope. These samples consisted of $\text{Mo}_{.68}\text{Ru}_{.32}$, $\text{Mo}_{.50}\text{Ru}_{.50}$ (displaying amorphous patterns at room temperature), and $\text{Mo}_{.82}\text{Ru}_{.18}$, which exhibited a crystalline pattern upon initial observation at room temperature. Both $\text{Mo}_{.68}\text{Ru}_{.52}$ and $\text{Mo}_{.50}\text{Ru}_{.50}$ showed a rapid transformation from the amorphous like diffraction pattern to a large grained crystalline pattern at approximately 800° K, or about one-

third the temperature of melting. The transformed structure for $\text{Mo}_{.50}\text{Ru}_{.50}$ was found to be a multi-phase structure on the basis of a standard ring diffraction pattern.

The structure for $\text{Mo}_{.68}\text{Ru}_{.32}$ was undetermined, as the grains were of sufficient size to produce single crystal patterns. A positive identification of a given structure would require diffraction patterns resulting from two different orientations. This requirement could be met utilizing a tilt stage to re-orient the sample for a second diffraction pattern, or, assuming that the sample was known to be of one phase, a second crystal would suffice.

However, this particular sample had a composition falling within a two phase region, which would preclude the use of two or more single crystals in the above manner with any assurance that they came from the same phase. If the structure were a metastable single phase, this objection would not apply; however, there is no way to guarantee, at this point, that the structure is in fact a metastable single phase. Tilt stage capabilities were not available on the hot stage used. Further work in this area was not pursued. A continuation of this work is suggested, not only for Mo-Ru, but also for the samples occurring in two phase regions of Mo-Zr, and Nb-Zr.

When $\text{Mo}_{.82}\text{Ru}_{.18}$ (crystalline at room temperature, with a grain size of about $50\text{\AA}$) was annealed, it showed no rapid transformation such as that seen for the above two samples. Rather, it retained its bcc structure, while showing a very small amount of grain growth.

IV. DISCUSSION

All determinations of the structures present at 4° K (upon deposition) presented in this work were hindered by a lack of in situ diffraction capability. Thus structural determinations are based on the structure present at room temperature after annealing from 4° K, on the T_c data for these systems at 4° K, on the observed resistance data during the anneal, and on previous work done by other authors under similar conditions and on similar systems.

Mader^{6,7,8} has reported the capability to stabilize an amorphous structure in a binary alloy up to and above room temperature when the composition falls within a miscibility gap of the phase diagram. Such results have been confirmed here for Nb-Zr binary alloy compositions within a miscibility gap, as well as for Zr-Mo and Mo-Ru compositions falling within two phase regions in general, the two phase region being bounded by either a solid solution or intermediate compounds.

The only system of these three to show an unambiguous amorphous appearing diffraction pattern is the $Zr_{.50}Mo_{.50}$ composition. All of the structures falling within the two phase regions of Nb-Zr and Mo-Ru show a diffraction pattern of three broad halo-like rings, which can be correlated with the first, third, and fourth diffraction rings for the face centered cubic structure, with the second ring missing. Such a pattern correlates with Mader's description of the structural changes which occurred in the process of transformation of a $Cu_{.46}Ag_{.54}$ alloy from an amorphous structure to a metastable fcc structure. In the course of this transformation, the second amorphous ring was observed

to split into two rings (fcc 220 and 311), followed by the splitting of the first ring into two rings (fcc 111 and 200), both occurring at a single well defined temperature. At this point very small grains of approximately 50 Å diameter were observed.

Based on these results by Mader,⁶ it would appear that the Nb-Zr and Mo-Ru samples may be in the initial stages of the transformation from the amorphous state to a metastable fcc structure - with the second ring already having split, but the first ring not yet having done so.

Two of the samples falling within the area of this discussion were annealed in the electron microscope, up to approximately 800° K. In neither case did the first ring split to complete the first four rings, as might be expected from Mader's⁶ results. Instead, the diffraction pattern remained unchanged until the range of 800° K, at which time both samples underwent a very rapid transformation to large grained crystalline structures.

The explanation as to why no further transformations to the metastable phase structure took place may rest in the fact that the transformation may be time dependent and the rate of anneal in the hot stage was simply too fast; i.e., a sufficient temperature was reached for a transformation to the stable structure before the transformation to the metastable fcc structure was complete. A second possible explanation for the split ring rather than a single ring in the amorphous pattern is that it may simply be representative of a slight increase in the amount of ordering, rather than an indication of an ensuing phase change to a metastable fcc structure. In this case further splitting of the first line would not be expected. In either case, the indication is that the structure as deposited was highly disordered or amorphous like.

At this point a very brief discussion of the type of diffraction

pattern which would be expected from an amorphous structure is in order. Any amorphous structure would experience some degree of short range order. Nearest neighbor effects arising from the presence of this short range order would result in the appearance of one or more diffuse appearing diffraction rings. The point at which the short range order becomes sufficiently long range to be considered microcrystalline, rather than amorphous, is ambiguous at the present time. Thus, as considered here, an amorphous structure is one which, in experimental terms, exhibits a diffraction pattern with a few broad halos that can not simply and uniquely be assigned to the diffraction lines of a crystalline structure, and which is also similar to that for a liquid. However, the same type of diffraction pattern results for a very fine microcrystalline structure.

It is possible to differentiate between the two structures using two different means available here, these being an observation of the resistance data and observation of the diffraction pattern upon annealing above room temperature. If the sample were originally amorphous, then the diffraction pattern would show a rapid change to a crystalline structure, at a well defined temperature, as the transformation took place, as well as showing a sharp drop in the resistance at the same temperature.

On the other hand, if the structure were originally microcrystalline, then the diffraction pattern would be expected to show a gradual sharpening of lines until a crystalline pattern was readily apparent. In addition, the resistance change would be gradual, corresponding to the annealing out of various defects and to grain growth.

Based on previous work (as discussed in the Introduction), it can be said that there is a correlation between a phase transformation

and a sharp resistance drop. Hence, for the bcc elements and their near alloys which show a sharp resistance drop at some point between 4° K and room temperature, it can be assumed that a phase transition has occurred. Based on the room temperature diffraction results it is apparent that the structures for all of these compositions underwent a change from either an amorphous or a metastable crystalline pattern to the normal stable bcc crystalline pattern. A transformation from a very fine microcrystalline pattern to a crystalline structure can be ruled out due to the presence of a sharp resistance change.

In order to differentiate between an amorphous or amorphous like structure and a metastable structure in the as deposited condition, it is necessary to resort to the observed T_c data. Contributions to the superconducting behavior can be attributed to two effects, the first being structural effects (band effects) and the second chemical effects. The T_c data is suggestive of the structural effects being reduced to a minimum, i.e., the data is essentially independent of the structures of the samples. Such a removal of structural effects would be consistent with the materials being deposited in a highly disordered state, possibly amorphous. Thus, by combining this data, with the presence of amorphous like structures for those compositions occurring in two phase regions, it can be said, with some confidence, that the structures in these cases (bcc near alloys) at 4° K, are amorphous also. The details of this explanation will be contained in a paper to be published by M. M. Collver and R. H. Hammond.¹

The minimum grain sizes observed by dark field micrography were in the range of 35 - 40 Å for pure ruthenium. Such a measurement does not preclude the existence of grains smaller than this, which may not have been apparent under the experimental conditions. Where grain sizes with

an estimated minimum of $10 \text{ \AA}$ - $20 \text{ \AA}$ are reported, principally for Nb-Mo alloys, the estimate was based on the existence of continuous diffraction rings exhibiting a bcc structure, as opposed to spotty rings which were observed when the grain size was in the approximate range of $50 \text{ \AA}$ and larger.

The results for Mo-Ru tend to confirm results by Mader⁶ in which he reported extending the range of solid solubility of Au-Co and Cu-Ag alloys by vapor deposition. However, the results for Mo-Ru, in addition to Nb-Zr and Nb-Mo, indicate that all samples (pure elements, solid solution alloys, and those samples occurring in two phase regions), with the possible exception of close-packed elements, can be deposited in the amorphous state; whereas Mader reports that only those in a two phase region can be so deposited, based on results for Cu-Ag and Co-Au. The results presented here are in agreement with those of several other authors for transition metals, notably Fujimi¹³ (Ti, Ni, Co, and Yt) and Bosnell⁵ (Ni), in that amorphous structures are formed -- though not in the range of stabilization claimed.

What these results indicate, then, is that only the degree of stability of an amorphous structure varies with the composition, rather than the ability to produce an amorphous structure. The least stability on a relative basis for a given system, as measured by the temperature of transformation, appears to occur for the pure elements and low concentration solid solution regions, with a maximum stability occurring toward the center of two phase regions.

Transformation temperatures (for the phase transformation from the amorphous to stable structure) of from 0.30 to $0.35 T_m$ have been reported for a number of systems by Chopra,¹⁵ and Madar⁶ in two phase regions, where T_m is the average melting point of the two components.

Transition temperatures approximating $0.3T_m$ were found for the two alloys falling in two phase regions and annealed above room temperature in the electron microscope. Transition temperatures significantly below this were found in all cases for the pure elements (bcc) and their near alloys, falling in solid solution regions, as opposed to what might be expected from previous work on 3d transition metals by Fujimi and Bosnell, where the amorphous structure was reported to be stabilized to room temperature. The differences here might be due to different vacuum evaporation conditions in terms of contamination, either in the system or the materials used.

For the hcp elements and near alloys, which showed a gradual irreversible resistance change upon annealing, in combination with a crystalline structure for the two examples so observed (Zr & Ru), a different explanation is needed. Previous work has shown that a phase transformation accompanies a sharp well defined resistance change; however, it has not been conclusively shown that a sharp well defined resistance drop must accompany a phase transformation.

If this assumption is made, then the possibility of a phase transformation for this particular case cannot be ruled out. In fact, since these samples are hcp, which is a close-packed structure, and an amorphous structure is nearly close-packed, it would seem quite plausible that a transformation could occur without greatly affecting the sample resistance (through a minimal mean free path change). The explanation for this effect is not entirely clear (in the near hcp alloys) and the above is merely a hypothesis at this point.

That a phase transformation for these alloys does in fact occur, or at the least is strongly suggested, is shown by T_c data in which the T_c measurements show a change between those made both before and after

annealing to room temperature. Such a change in the T_c value is indicative of a phase transformation. Similar changes in T_c were observed for the bcc and near bcc alloys, where a phase change is strongly indicated by the observed resistance data.

It has been observed that various high temperature metastable phases occur in the process of transforming an amorphous phase to the expected stable phase, according to the Ostwald rule. The Ostwald rule states that a system undergoing reaction proceeds from a less stable state through a series of increasingly more stable intermediate states to reach the final equilibrium state. The occurrence of these metastable states would usually depend on the presence of high temperature phases for a particular system, and on the relative stability of the given phase (the transformation might occur too rapidly to identify).

No metastable states were observed for those samples which underwent a phase transformation below room temperature (i.e., only one phase transformation indicated by the resistance changes). The two samples which were annealed in the electron microscope above room temperature both transformed to phases which are currently unidentified, and which may be metastable. There are indications that these two compositions occurring in the two phase region and having a near amorphous structure as observed at room temperature may go through a metastable fcc phase prior to the high temperature transformation. However, such a conclusion, as previously discussed, is not clear due to the rapidity with which the samples transformed during further annealing.

Finally, impurity stabilization is not considered to be a problem in explaining the amorphous structures occurring upon deposition because of the high purity of materials used, the relatively high rates of deposition ($\sim 200 \text{ \AA/sec}$), and the relatively high vacuum (5×10^{-8} torr). This point is important when reviewing past literature.

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FIGURE CAPTIONS

- Fig. 1. Diffraction pattern for $\text{Nb}_{.87}\text{Zr}_{.13}$ showing a characteristic pattern observed for bcc elements and their near alloys.
- Fig. 2. Diffraction pattern for $\text{Nb}_{.78}\text{Mo}_{.22}$. A minimum grain size of from 10-20 $\text{\AA}$ is estimated from these patterns, based on experimental observations of spotty rings from grains of a size near 100 $\text{\AA}$, as opposed to the continuous rings observed here.
- Fig. 3. Diffraction pattern for $\text{Mo}_{.68}\text{Ru}_{.32}$ showing a characteristic amorphous like structure for compositions falling in two phase regions.
- Fig. 4. Temperature-vs-resistance curve for $\text{Zr}_{.13}\text{Nb}_{.87}$. This is a characteristic curve for bcc elements and near alloys which exhibit a crystalline diffraction pattern at R. T.
- Fig. 5. Temperature-vs-resistance curve for $\text{Mo}_{.10}\text{Ru}_{.90}$. This curve is characteristic of those for hcp elements and near alloys which exhibit a crystalline diffraction pattern at R. T.
- Fig. 6. Temperature-vs-resistance curve for $\text{Mo}_{.68}\text{Ru}_{.32}$. This is a characteristic curve for compositions falling in two phase regions and exhibiting amorphous like diffraction patterns.

TABLE CAPTIONS

- Table 1. Compilation of data for bcc elements and near alloys (Nb-Zr)
- Table 2. Compilation of data for bcc elements and near alloys (Nb-Mo)
- Table 3. Compilation of data for bcc elements and near alloys (Mo-Ru)
- Table 4. Compilation of data for hcp elements and near alloys (Zr, Ru, and Mo-Ru)
- Table 5. Compilation of data for compositions falling in two phase regions and displaying amorphous like diffraction patterns (Nb-Mo, Nb-Zr, and Mo-Ru)

XBB 719-4356

Figure 1.

XBB 719-4355

Figure 2.

XBB 719-4353

Fig. 3

-33-

XBL 719-7245

Figure 4.

XBL 719-7247

Figure 5.

XBL 719-7246

Figure 6.

TABLE I

Sample Number	Composition (at.%)	Structure	Grain Size	T at which Ω drop occurred	$T_c(4^\circ K)$	T_c after anneal
107-2	Nb _{0.97} -Zr _{0.13}	bcc	70-3000 Å	150-170 °K	5.42 $\begin{smallmatrix} +.12 \\ -.04 \end{smallmatrix}$	7.35 $\begin{smallmatrix} +.18 \\ -.09 \end{smallmatrix}$
108-3	Nb _{0.925} -Zr _{0.075}	bcc	133-1000 Å	100-120 °K	5.9 $\begin{smallmatrix} +.16 \\ -.07 \end{smallmatrix}$	8.18 $\begin{smallmatrix} +.17 \\ -. \end{smallmatrix}$
108-2	Nb _{0.945} -Zr _{0.055}	bcc	167-1000 Å	110-130 °K	5.66 $\begin{smallmatrix} +.11 \\ -.05 \end{smallmatrix}$	7.54 $\begin{smallmatrix} +.08 \\ -.04 \end{smallmatrix}$
108-1	Nb _{0.97} -Zr _{0.03}	bcc	333-2000 Å	90-100 °K	5.91 $\begin{smallmatrix} +.14 \\ -.15 \end{smallmatrix}$	7.5 $\begin{smallmatrix} +.27 \\ -. \end{smallmatrix}$

TABLE II

Sample Number	Composition (at.%)	Structure	Grain Size	T at which Ω drop occurred	$T_c(4^\circ K)$	T_c after anneal
106-3	Nb _{0.91} -Mo _{0.09}	bcc	10 Å min.	----	6.06 $\begin{smallmatrix} +.03 \\ -.2 \end{smallmatrix}$	5.79 $\begin{smallmatrix} +.13 \\ -.39 \end{smallmatrix}$
101-4	Nb _{0.76} -Mo _{0.22}	bcc	10-100 Å min.	40 - 70 °K	5.72 $\begin{smallmatrix} +.10 \\ -.20 \end{smallmatrix}$	2.0 $\begin{smallmatrix} +.10 \\ -.10 \end{smallmatrix}$
101-5	Nb _{0.30} -Mo _{0.70}	bcc	10 Å min.	----	7.10 $\begin{smallmatrix} +.15 \\ -.30 \end{smallmatrix}$	2.6 $\begin{smallmatrix} +.4 \\ -.1.0 \end{smallmatrix}$
101-2	Nb _{0.02} -Mo _{0.98}	bcc	10-333 Å min.	65 -110 °K	8.2 $\begin{smallmatrix} +.1 \\ -.3 \end{smallmatrix}$	< 1.7

TABLE III

Sample Number	Composition (at.%)	Structure	Grain Size	T at which Ω drop occurred	$T_c(4^\circ K)$	T_c after anneal
102-2	Mo _{0.89} -Ru _{0.11}	bcc	50-1000 Å	130-200 °K	8.9 ^{+0.1} -0.05	7.02 ^{+0.28} -3.0
104-4	Mo _{0.82} -Ru _{0.18}	bcc	100-300 Å	110-130 °K	9.4 ^{+0.07} -0.05	6.18 ^{+0.95} -0.1

TABLE IV

Sample Number	Composition (at.%)	Structure	Grain Size	T at which Ω drop occurred	$T_c(4^\circ K)$	T_c after anneal
110-5	Zr	hcp	200- 1500 Å	----	3.26 ^{+0.08} -0.37	<1.72
112-1	Mo _{0.10} -Ru _{0.90}	---	---	----	2.62 ^{+0.13} -0.43	<1.7
104-2	Mo _{0.03} -Ru _{0.97}	---	---	----	<1.7	---
103-4	Mo _{0.03} -Ru _{0.97}	---	---	----	<1.7	---
103-3	Ru	---	---	----	<1.7	---
112-4	Ru	hcp	35-40 Å	----	<1.7	<1.7

TABLE V

Sample Number	Composition (at.%)	Structure	Grain Size	T at which Ω drop occurred	$T_c(4^\circ K)$	T_c after anneal
102-3	Zr.85 -Mo.15	2 - ring diffuse	---	----	4.14 $\pm .20$ -.10	3.86 $\pm .10$ -.20
107-5	Zr.40 -Nb.60	3 - ring diffuse	---	----	4.88 $\pm .06$ -.06	3.31 $\pm .05$ -.05
107-4	Zr.33 -Nb.67	3 - ring diffuse	---	----	4.58 $\pm .14$ -.06	2.49 $\pm .09$ -.05
104-3	Mo.68 -Ru.32	3 - ring diffuse	---	----	8.20 $\pm .05$ -.05	8.68 $\pm .05$ -.05
105B-5	Mo.50 -Ru.50	3 - ring diffuse	---	----	7.75 $\pm .05$ -.05	7.65 $\pm .05$ -.05

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