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by

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RADIATION DAMAGE IN Nb and Ta

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TECHNICAL PROGRESS REPORT

During the year work has proceeded in the following areas:

- A. General Annealing Behavior Survey Completed (See enclosed reprint.)
- B. Second and Improved Ultrahigh Vacuum System Constructed for Sample Purification Work.
- C. Sample Purity.
- D. High Temperature Annealing Behavior.
- E. Concentration Dependence
- F. Threshold Measurements

These items are described in detail below.

The Vacuum System

The vacuum system (Fig. 1) was designed and built keeping in mind these three main features; (a) Pressures of $1.0 \cdot 10^{-8}$ mm Hg should be routinely obtainable; (b) It should be possible to introduce any atmosphere having a partial pressure of $1.0 \cdot 10^{-3}$ or less into the sample chamber; (c) Easy mounting and removal of samples in the vacuum chamber should be possible.

(a) The design incorporates the following features: All 300 Series stainless steel construction; metal to metal seal on the ultrahigh vacuum side of the last cold trap; two cold traps each equipped with liquid N_2 cooled anti-creep baffles of a somewhat novel design; two oil diffusion pumps; Ti sublimation pump mounted right below but baffled from sample chamber; a sufficient number of current feedthroughs, and facilities for baking out the sample chamber, ion gauge tube, and

sublimation pump. A vacuum of $8.0 \cdot 10^{-9}$ was obtained on the first run measured with a CVC nude ionization gauge. Only 10 hours of baking out and pumping down was required to obtain this vacuum.

(b) A CVC gate valve and a Heraeus Engelhard microvalve were purchased to valve off the system at the top of the last oil diffusion pump and bleed any partial atmosphere into the sample chamber part of the system.

(c) Varian ultrahigh vacuum current feedthroughs were purchased on which to mount the samples so that their resistances could be monitored.

Sample Preparation and Purification

A great amount of work has been done during the last year on preparing and purifying thin wire samples of Ta and Nb. The resistance ratios ($R_{\text{Room T}}/R_{10^{\circ}\text{K}}$) of Ta and Nb as delivered by MRC are in the range of 10 - 20 for wires having 2 mil diameter. Two mil wires are virtually impossible to purify by any of the conventional methods such as zone refining. Another problem that has to be considered is that both Ta and Nb are excellent "getters" when heated. This necessitated (A) the designing and building of a suitable ultrahigh vacuum system as described above, (B) an investigation as to the kinds and nature of the impurities, and (C) the working out of a feasible method of purification.

(B) Nature and types of impurities.

There are essentially four types of impurities and defects one has to be concerned with; (a) Gases in solutions; (b) surface contamination; (c) substitutional impurities; (d) dislocations and grain boundaries.

(a) Gases in solution are believed to be the main impurities but

are also the easiest ones to get rid of. Even at room temperature Ta and Nb have a relatively high equilibrium concentration of gases in solution and it is believed that during the preparation of the wire at MRC work such as the drawing of the wires has been done at elevated temperatures causing a large concentration of gases in solution. These can be removed simply by heating the wires up to 2200° - 2600°C in a good vacuum system and outgassing.

(b) Surface contamination has been incurred during drawing, handling and pumping down the vacuum system. An oxide layer will also form during storage. These impurities will be mainly iron from the drawing and carbon from handling and diffusion pumps. Some of these impurities will diffuse relatively far into the wire and on the scale of a 2 mil wire the surface layer will be relatively thick.

(c) Substitutional impurities are impurities left after the zone refining at MRC consisting mainly of Ta in Nb and vice versa plus W and Mo. Also some Fe will be present. These are virtually impossible to get rid of. C is in addition found as a substitutional impurity.

(d) Grain boundaries and dislocations are caused by cold work such as drawing the wires and mounting the samples. These will to a large extent anneal out at a sufficiently high temperature.

C. Method of purification¹

The procedure can be divided roughly into three parts; (a) making and mounting of samples; (b) annealing of samples in an O_2 atmosphere of 10^{-4} - 10^{-5} mm Hg partial pressure at 1300 - 1800°C ; (c) annealing of the samples in a vacuum of 1.0 - $3.0 \cdot 10^{-8}$ at temperatures near the melting point.

(a) The samples are made having a total length of about $1\frac{1}{2}$ " with potential leads of the same material spot welded on about $\frac{1}{4}$ " apart yielding an active sample about $\frac{1}{4}$ " long. Then the sample current and potential leads are spot welded onto the Cu vacuum feedthrough leads. Finally the feedthrough is mounted on the vacuum chamber port such that the sample is hanging vertically from the Cu feedthrough leads.

(b) The sample is annealed for one minute at $1300 - 1800^{\circ}\text{C}$ at an oxygen partial pressure of $10^{-4} - 10^{-5}$ to cause the Fe and C impurities to form oxides. Oxides are relatively easy to boil off while substitutional Fe and C are very highly bound. The titanium sublimation pump is cycled about once every hour in order to maintain a particularly low partial pressure of oxygen in order to facilitate the oxide evaporation.

(c) Then the sample is outgassed at gradually increasing temperatures by passing a current through them such that a good vacuum is maintained. ($< 5 \cdot 10^{-8}$) Finally the samples are baked near to their melting points and annealed for up to 48 hours maintaining vacuum $< 3.0 \cdot 10^{-8}$ mm at all times. This gets rid of dislocations and grain boundaries and will also boil off all gases in solution and some substitutional impurities.

As of now Ta samples having a resistance ratio of about 400 ($R_{\text{Room T}}/R_{4.5^{\circ}\text{K}} \approx 400$) and Nb samples having 200 have been produced.

A paper is currently being prepared on the purification process.

High Temperature Annealing Behavior

In order to study the annealing above 80°K as revealed in the

survey described in the enclosed reprint a cryostat for 80°K irradiation was constructed (see Figure 2). A constant temperature bath and controller were constructed using Liquid Propane as the bath medium (see Figure 3). A special He cryostat for dunking the sample holder (so that measurements could be made at He temperatures) was also constructed (see Figure 4). The experimental plan was as follows:

- A. Measure resistance vs. temperature for undamaged samples from 10°K to 20°K in the dunking cryostat. Although the system was designed to achieve temperature control by balancing heat input from a resistance heater with cooling by cold He gas from the coil, it was found that sufficient stability was obtained by merely holding the sample holder a little way above the liquid He surface.
- B. Place the sample holder in radiation jig and irradiate with the whole assembly immersed in liquid N_2 and the holder filled with He gas. A total damage equal to the residual resistivity was planned.
- C. Remove the sample holder from the jig and place it in liquid N_2 . The holder is massive enough that its heating rate is $\sim .01^{\circ}\text{K}/\text{sec}$.
- D. Dunk the sample holder in the He cryostat and measure the total damage obtained.
- E. Remove the sample holder from He and dunk it in liquid nitrogen.
- F. Remove the sample holder from the liquid N_2 and dunk it in the constant temperature bath for a given time.
- G. Remove the sample holder from the bath and dunk it in liquid N_2 .

- H. Remove the sample holder from the liquid N_2 and dunk it in He. Measure the new resistance. The temperature of the holder when in the He cryostat was monitored by a AuCo vs Cu difference thermocouple between the liquid He and the holder. Our previous calibration (Step A) was then used to determine the damage remaining.
- I. Remove the sample holder from the He and dunk it in liquid N_2 .
- J. Repeat steps F - I for bath times of 2, 4, 8, 16, 32, 64 minutes at the same bath temperature.
- K. Repeat steps F - J for a series of bath temperatures.

The entire system was checked out and a trial radiation run was made with as received (unannealed) samples. A damage rate comparable to that obtained in the enclosed reprint was found. However when the experiment was performed with very pure well annealed samples an extremely low damage rate was obtained. In fact, a rate so low that the experiment was discontinued temporarily while that effect is investigated more thoroughly. The most obvious possibility is that free migration occurs below 80°K and that as a result the free interstitial concentration is always small. Then the damage observed would be the result of whatever interstitials were trapped by impurities or dislocations. In the unannealed samples the dislocation density is quite high and thus trapping is important resulting in a high damage rate. A careful study of the damage rate versus sample purity at 80°K when compared with the damage remaining at 80°K from a 10°K irradiation should provide considerable insight into interstitial clustering and trapping. This study is presently being run.

From the standpoint of studying the high temperature stages it is

clear that the radiation must be performed below the free migration point if one is to see any property intrinsic to the material as opposed to impurities and dislocations which may be present. Thus this aspect of the problem has been set aside until the concentration experiment has been completed and the free migration point established.

Concentration Dependence

A study of the concentration dependence of the annealing processes of interstitials in Ta and Nb that was proposed in last year's program is currently being completed. The final radiation run is scheduled to be made at the end of March.

During this run three pairs of Ta and Nb samples will be irradiated for varying lengths of time. In addition a pair of completely shielded samples will be monitored as "controls". Due to the large number of samples four more constant current supplies have been built. After having completed the irradiation the samples will be annealed isothermally in the temperature region from 12°K to 80°K. In order to minimize the uncertainties due to temperature fluctuations and to ensure the best possible absolute and relative resolution of the annealing processes as a function of temperature, measurement and stability of the temperature is of the utmost importance. Thus a platinum resistance thermometer has been purchased from Honeywell and is currently being calibrated at the National Bureau of Standards. In addition a considerable effort has been made to build an electronic temperature controller. This device will automatically analyze the output from the resistance thermometer mounted on the sample holder, compare it to a standard signal corresponding

to the desired temperature and feed the amplified difference into the sample heater control lowering or raising the temperature until it coincides with the desired one. This controller has been built and tested. A temperature fluctuation of less than $5 \cdot 10^{-3} \text{ } ^\circ\text{K}$ is expected.

The procedure for mounting samples has been improved during the last year. These improvements are beneficial in two ways; First, the cold work of the annealed samples is reduced to an absolute minimum and secondly, better thermal contact with the sample holder is obtained such that the beam current can be increased giving a larger damage rate. The procedure is as follows (shown schematically in Figure 5): The sample leads and copper leads are spot welded onto a one mil stainless steel foil that has been cut such as to expose the active sample parts to the beam. Then the foil is glued onto a bakelite backing. Following this part of the foil is cut away to electrically insulate the potential and non-common current leads from each other. Finally another sheet of bakelite is glued on top, leaving only the active parts of the samples exposed. This way one can make a "sandwich" with several layers of samples. The last step is to fasten this "sandwich" to the sample holder and solder the common current part of the foil to the holder giving excellent thermal contact.

Threshold Measurements

During the year we have succeeded in producing the oriented, .002" thick single crystal samples needed.

¹We are greatly indebted to Dr. Richard E. Reed at Oak Ridge National Laboratories for information and suggestions resulting from his own work on the purification of Nb.

Figure 1

Diagram of Ultra High Vacuum System

Figure 2

LIQUID NITROGEN RADIATION JIG

Figure 3

ISOTHERMAL ANNEALING

Scale 1" = 2"

Temperature Range
-180°C to 200°C

Temperature Control
± .05°C

Figure 4

High Temperature Annealing Cryostat

Figure 5