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NASA TM X-67868

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QUENCHING OF VACANCIES INTO MOLYBDENUM

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TECHNICAL PAPER proposed for presentation at
Discussion Meeting on Defects in Refractory Metals
Mol, Belgium, September 20-22, 1971

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E-6414

INTRODUCTION

Measurement of the properties of point defects in the b. c. c. refractory metals is vital to the understanding of radiation effects, diffusion and the mechanical behavior of these high temperature materials. Direct quenching and subsequent annealing to determine vacancy formation energies, E_f^v, and migration energies, E_m^v, has proved most successful for many f. c. c. metals. However, with the b. c. c. metals the expected small ratio E_m^v/E_f^v and the greater possibility of contamination lead to severe experimental problems. The first difficulty can be overcome with rapid quenching and extrapolation techniques. The problem of maintaining the high purity required for an unambiguous interpretation of quenching experiments with b. c. c. metals appears to have been solved by a method involving quenching into the ultrapure environment of liquid helium II. This technique proposed by Rinderer and Schultz[1] was used by Schultz[2] to determine for tungsten, $E_f^v = 3.3$ eV and a vacancy fraction at melting, $(n_v/N)_{m.p.} = 1 \times 10^{-4}$. Gripshover, Khoshnevisan, Zetts, and Bass[3] later extended these measurements on W by varying the quench rate and extrapolating to infinite rate. Their value of $E_f^v = 3.6$ eV was in reasonable agreement with the earlier work and lends strong credence to the method.

Some preliminary attempts to quench vacancies into molybdenum using the helium II technique were made by Gripshover.[4] He reported considerable scatter in his data, however, and no estimate of E_f^v was made.

Other studies of vacancy quenching in Mo have been reported. Meakin, Lawly, and Koo[5] used an indirect microscopic technique to determine the vacancies quenched into Mo foil. They reported $E_f^v = 2.5$ eV and $(n_v/N)_{m.p.} = 5\times10^{-5}$. Kraftmakher,[6] using specific heat measurements, found nearly the same formation energy for Mo, $E_f^v = 2.24$ eV, but their vacancy fraction at melting was three orders of magnitude higher.

More recent measurements by Evans,[7] however, served to question these results. Using a method in which thin (0.050 mm) foils were directly quenched into mercury, Evans reported that he was unable to quench vacancies in Mo. With even thinner foils he did observe erratic increases in the resistivity, but he ascribed these to dislocations formed during the quench. Microscopic examination of these quenched specimens confirmed the presence of high dislocation densities. He estimated his quench rates as greater than 10^5 K/sec. Accordingly, Evans was led to suggest that the previous work on vacancy quenching in Mo and also that reported by Gripshover et al.[3] and Schultz[2] on W was due to impurity effects. These experiments by Evans were prompted by earlier experiments by Evans and Eyre,[8] and Burke, Kothe and Werth[9] who found less than 1 ppm of vacancies were quenched into their thicker molybdenum samples. Evans,[7] however, suggests that in both of the experiments the relatively low quenching rates associated with thick samples may preclude vacancy quenching.

Our experiment is an attempt to resolve this disparity of results for Mo by a systematic study of the variables of quenching environment, rate, and impurity effects. In this paper preliminary results on quenching into a helium II environment are presented. The quenched-in resistance measured will be discussed in terms of possible causes. Further work will extend the experimental parameters to both higher and lower quench rates, and annealing studies will be made to aid in the identification of the quenched-in species.

EXPERIMENTAL

The molybdenum samples used in this work were fabricated from the Westinghouse Company zone refined monocrystalline material having a resistance ratio ($R_{273K}/R_{4.2K}$) of greater than 10 000. Immediately after drawing to 0.050 mm the ratio was ~15. Just prior to use, the samples were etched in a water solution of $K_3Fe(CN)_6$ and KOH to remove surface contamination. They were then washed in NH_4OH, rinsed in distilled water and dried. Similarly prepared 0.012 mm potential leads were spot welded to the sample about 2 cm apart and the assembly was secured into place in the helium dewar.

Repeated anneals just above the liquid helium II surface resulted in an increase of the resistivity ratio to around 1700. The first anneal was usually 45 minutes at about 2300 K, followed by slow cooling. Successive 5 minute anneals served to indicate when the minimum resistance was reached. The helium gas pressure during these anneals did not exceed 0.6 torr.

The wire samples were joule heated using a regulated dc power supply. The temperatures were obtained by measuring the sample resistance using the data of Worthing.[10]

After usually 1 to 2 minutes at temperature, the wire was quenched by interrupting the heating current. The cooling curve was recorded photographically from an oscilloscope trace. The reported quench rates correspond to the initial slope of the temperature (voltage)-time curve. The quenches reported here were made just above the liquid helium surface. They ranged from about 2500 to 5000 K/sec. Quench rates an order of magnitude higher are expected from quenches into the liquid.

The resistance at room temperature and at 4.2 K were obtained using standard potentiometric techniques providing a sensitivity of approximately 1×10^{-12} Ωcm.

Errors in the quenched-in resistance were estimated to range from about 12 percent for the lowest temperature quench to about 3 percent for the highest temperatures.

RESULTS AND DISCUSSION

The results from quenches of 0.050 mm molybdenum wires are shown in figure 1. These data were taken over a temperature interval from 1660 K to 2130 K at quench rates around 4×10^3 K/sec. While the range of quench rates is too narrow to allow extrapolation to infinite rate, we can at this time draw several important conclusions from the data.

1. We do not see the scatter that characterized the data of references 4 and 7. The data points fit an Arrhenius plot quite well. The slope of the curve gives an energy of 1.7 eV which is substantially greater than that determined from the best fit of the data of Gripshover.[4] This energy is too high to be explained by the dissolution of C, N, or O, which show heats of solution near 1 eV.[11] Moreover, if Mo resembles W in its quench rate dependence (cf. ref. 2) then higher quench rate experiments (now in progress) may well increase this 1.7 eV energy.

2. The quenched-in resistivity in this study is more than an order of magnitude larger than that found by Evans with foils of similar thickness (0.050 mm). The attainment of higher quench rates in our experiments may increase this difference.

3. Evans has suggested that the tungsten quenching data of Schultz[2] and Gripshover et al.[3] might be explained by the dissolution of helium into the metal. If helium were to equilibrate in solid solution with the metal, according to Gibb's phase rule, there should exist three degrees of freedom for the helium. The concentration of helium, therefore, will depend on both temperature and pressure. In both our experiments and those of Gripshover, et al.[3] on W the pressure of helium was allowed to vary over a factor of 5. In both cases,

there was no corresponding variation observed in the quenched-in resistance at constant temperature. Moreover, in some preliminary experiments performed to establish our experimental technique we quenched 0.050 mm tungsten wires in helium gas. We obtained similar values to those of reference 3 where thinner wires were quenched in liquid helium II, again at pressures quite different from ours. This absence of pressure dependence indicates that dissolved helium is not responsible for the quenched-in resistance in these experiments.

In summary, we see nothing in out data to indicate that the quenched-in resistance is due to other than vacancies. We cannot, however, give values of E_f^v, E_m^v, and $(n_v/N)_{m.p.}$ at this time. While our data appears consistant with similar studies on tungsten,[2,3] we are clearly in disagreement with the negative findings of Evans.[7] Possibly unknown impurity effects or quenching strains may contribute in that experiment. Evans[7] comments that quenching strains have indeed produced dislocations in his samples. Jackson[12] points out that such defects, acting as sinks, can reduce the quenched-in vacancy concentrations far below that characteristic of an unstrained sample. This is especially true of hydrodynamic drag strains which occur with thin samples in dense quenching media. Further work is certainly indicated.

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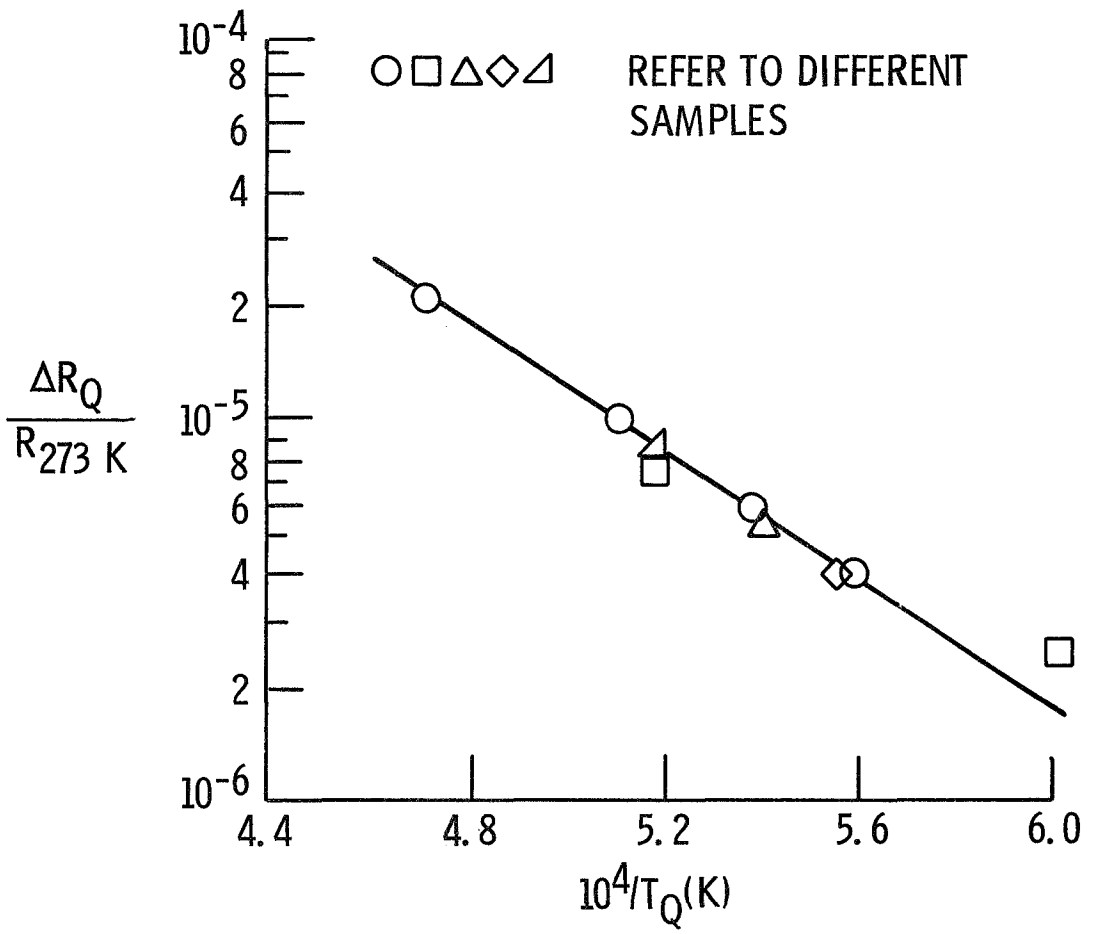

Figure 1