Microstructural Studies of Hydrogen and Deuterium in BCC
Refractory Metals

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During this contract period the following activities have been of principal concern:

1. X-Ray Facility

The X-ray laboratory was completed with facilities for $\text{CuK}\alpha$ and $\text{MoK}\alpha$ scattering. In particular we have installed two quite versatile set-ups including curved Ge monochromators to produce $\text{CuK}\alpha_1$ and $\text{MoK}\alpha_1$ for high resolution work with our two teletype-controlled Rigaku diffractometers. We have also constructed a moderate ($<250^\circ\text{C}$) - temperature vacuum furnace for studies of hydride formation and metal-hydrogen phase transitions. All of the electronics and detection apparatus are interchangeable between the units and both $\text{MoK}\alpha_1$ and $\text{CuK}\alpha_1$ studies are now routinely performed.

2. H in Ta (X-Ray Scattering)

A longer paper on H-Ta was completed by Metzger in which the details of the displacement field surrounding the H interstitial in Ta were described. This work was summarized at the 2nd International Congress on Hydrogen in Metals, Paris, June 7-11, 1977 and appears in the Congress Proceedings. A major conclusion of this work is that the metal atom displacements due to dissolved hydrogen can be treated as a linear superposition of the displacements due to a single interstitial defect up to, at least, a concentration $(\text{H}/\text{Ta}) = 0.111$. In addition, as with H - Nb, the displacement field about the tetragonal defect is cubic beyond, say, the first or second neighbor shell. This is a surprising result which should ultimately tell us a great deal about the fundamental bonding interaction between H(or D) and the metal lattice.

3. Order-Disorder in V_2D

Several large crystals of vanadium (V) were loaded with deuterium (D) by D. Westlake of Argonne to the concentration V_2D ($D/V = 0.500$) both under applied stress and unstressed. The ordering phase transition at $T_c \approx 130^\circ C$ is from BCC to monoclinic (pseudotetragonal) as the deuteriums occupy alternate octahedral sites along the tetragonal c axis. The result of this ordering of D atoms is to induce in the V lattice a modulation along, say, $\langle 101 \rangle$ with the same period as the ordered D superlattice. This modulation superstructure permitted us to measure with X-rays, for the first time, the detailed disordering in V_2D and to establish the thermodynamic order of the phase transition unambiguously as first order.

Neutron scattering was also performed at Argonne in which, in contrast to the X-ray study, only the D atom positions were examined. Our preliminary results indicate a difference between the neutron-determined order parameter and the nominally equivalent X-ray data. This leads us to more insight about the induced V atomic displacements and to the nature of the disordered sites for the D atoms that leave their ordered octahedral positions.

Finally our preliminary examination of the more macroscopic aspects of the ordering transition leads us to a consideration of domain formation and micro-twinning by which the transformation strains are accommodated. The hydride, of course, is extremely brittle while the disordered α phase is not. It is our feeling that the embrittlement is directly related to these macroscopic strains which lend the transition a similarity to many martensitic transformations.

4. D in Ta (neutron scattering)

This study was performed at Brookhaven with Dr. S. M. Shapiro on a large Ta crystal loaded with D to $D/Ta = 0.13$. Unfortunately, the original vacuum degassed crystal had an unacceptable mosaic structure (neutrons, looking at the whole crystal, are much better for determining this than X-ray scattering off the crystal surface) with a spread of nearly 1° among the diffracting blocks. Although this crystal will be replaced, preliminary neutron data were collected along the $[111]$ direction between $(0.5, 0.5, 0.5)$ and $(1.5, 1.5, 1.5)$. We were especially interested in the purely elastic scattering associated with the displacement field of the D defects. In this case, however, we wished to observe an "anomalously" large scattering near $2/3 [111]$ associated with an induced structural softness at this omega-phase wave vector. The results showed a nearly uniform weak scattering with an anomalous drop at about $[1.33, 1.33, 1.33]$ which is an equivalent omega position. The origin of this is not clear and we shall pursue it further.

5. Positron Annihilation in H-Ta

Several crystals of the orientation $[100]$, $[110]$, and $[111]$ have been oriented and cut, are currently being degassed and will then be loaded to $H/Ta \approx 0.10$. Crystals both with and without H will be sent to Professor Stephan Berko at Brandeis University for the positron measurements. Through the work of Metzger and Peisl we know that below $H/Ta = 0.11$ the H atoms can be considered randomly distributed and acting as single defects. These samples are therefore ideal for the positron annihilation studies of the Fermi surface because there is no complication of clustering or ordering of impurities. The positron work

will be undertaken during the coming year.

Summary

In our microstructural program on H and D in the Group VB metals we have studied successfully both the atomic displacements and elastic interactions in dilute solutions and the ordering transition in a more concentrated alloy (V_2D). The influence of D in replicating or imitating a structural phase transition, i.e. the omega phase, has been studied in a preliminary way with elastic neutron scattering and will receive more attention. Finally samples are about ready for the proposed positron work in which we shall investigate basic electronic structure of a typical metal-hydrogen alloy.

Published Papers

1. T. H. Metzger and J. Peisl, "Diffuse X-ray Scattering From the Displacement Field of Hydrogen in Nb and Ta," Proceedings, Second Int'l Congress on Hydrogen in Metals Paris, 7-11 June (1977). *Reviewed*
2. H. Metzger and H. Peisl, "Huang Diffuse X-ray Scattering from Lattice Strains in High-Concentration Ta-H Alloys," J. Phys. F 8, 391 (1978). *Reviewed*
3. H. Metzger, H. Jo, S. C. Moss and D. Westlake, "Single Crystal X-ray Study of the Superstructure Modulation and Long-Range Order in V_2D ," Phys. Stat. Sol (a), 1978 (in press). *Reviewed*

Talks Presented - S. C. Moss

1. "Neutron Studies of Pretransitional Fluctuations Above Structural Transitions in Metals", invited talk: Conference on Order-Disorder in Solids, Paris, 4-8 July, 1977. J. Physique, 1978 (in press).
2. "X-ray Scattering from H in bcc Metals", Corporate Research Laboratory, EXXON Corp, Linden N. J. - fall 1977.
3. "Structure of H and D in bcc Metals", Physics Colloquium, Rice University, Spring 1978.
4. "X-ray Scattering from H and D in bcc Metals" Colloquium, Institute of Materials Science, NBS Spring, 1978.
5. "X-ray Study of the Superstructure Modulation and Long-Range Order in V_2D ," (with H. Metzger, H. Jo and D. Westlake) contributed paper, March meeting, APS Washington, D.C. (1978).