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AEC
RESEARCH
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REPORT

**PACIFIC NORTHWEST LABORATORY
MONTHLY ACTIVITIES REPORT
FEBRUARY 1966**

ON

**AEC DIVISION
OF
RESEARCH PROGRAMS**

MARCH, 1966

BATTELLE-NORTHWEST

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RICHLAND, WASHINGTON

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This report contains information of a preliminary nature prepared in the course of work under Atomic Energy Commission Contract AT(45-1)-1830. This information is subject to correction or modification upon the collection and evaluation of additional data.

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PACIFIC NORTHWEST LABORATORYMONTHLY ACTIVITIES REPORTFEBRUARY 1966AEC DIVISION OF RESEARCH PROGRAMS - R. S. PAULACTINIDE ELEMENT CHEMISTRY - F. E. VoilandSPECTRAL STUDIES OF ACTINIDE AND LANTHANIDE COMPLEXES

Studies of the electronic absorption spectra of actinide complexes have been underway for several years as part of the general program of developing an understanding of the chemistry of the actinides. Of particular importance are complexes of octahedral symmetry. Because of the obvious electronic structure relation as well as for practical experimental reasons analogous complexes of the lanthanides are also being studied.

A compound assigned the formula $[(C_6H_5)_3PH]_3PuCl_6$ was prepared but has not yet been analyzed. This assignment is based on the preparative technique (used for the corresponding lanthanide compounds) and its very weak color which is consistent with an octahedral complex with a center of inversion. The absorption spectrum has not yet been obtained but the solid salt is a grayish (almost white) crystalline precipitate, has a very different color from the Pu(III) aquo ion, and is much less intensely colored than the aquo ion or $PuCl_3$. A special cell will be used to avoid air contact as the complex is very easily oxidized to $PuCl_6^{2+}$.

Samples of $(C_2H_5)_2NH_2Cl$ and $[(C_2H_5)_2NH_2]_2UO_2Cl_4$ were prepared to see if the nitrogen NMR resonance could be detected for such solid salts. No success was obtained. Samples of mixed crystal $[(C_6H_5)_3PH]_3LaCl_6 - [(C_6H_5)_3PH]_3NdCl_6$ were prepared with varying La/Nd ratio for magnetic susceptibility measurements.

A paper on Spectra of the Lanthanide Hexahalide Complexes jointly authored by J. L. Ryan and C. K. Jørgenson (Cyanamid, Geneva, Switzerland) has been submitted to J. Phys. Chem.

X-RAY DIFFRACTION

The determination of crystal structure gives direct information on molecular structure, e.g., bond distances, but also is important to the interpretation of the electronic spectra of the compounds. The first compound being studied, following the setting up of the equipment for single crystal structure determination, is uranyl methane sulfonate $UO_2(CH_3SO_3)_2 \cdot H_2O$.

The collection of additional intensity data for the crystal $UO_2(CH_3SO_3)_2 \cdot H_2O$ from the HK5, HK6 and HK7 layer lines has been completed. The additional 362 reflections will reduce the series termination error in the Fourier projection and yield a better resolution of the light atoms in the presence of the heavy atom, uranium.

Experiments are underway to grow single crystals of several of the actinide and lanthanide hexahalide complexes.

WIDE-LINE nmr STUDIES

An excellent approach to the investigation of the existence and nature of the so-called cation-cation complexes^(*) is through measurement of the nmr

(*) J. C. Sullivan, Inorg. Chem. 3, 315 (1964).

signal of one member of the complex. Indium and gallium are good candidates for forming these complexes and have good nmr signals. It is intended to examine the actinide elements, e.g., neptunium, but the initial experiments will be carried out with the transition elements.

The linewidth of the ~ 0.8 M In(III) and ~ 0.7 M ClO_4^- solution has been remeasured as 723 ± 30 cps on the basis of a recalibration of the scanning field. The addition of both Fe(III) and Cr(III) in concentrations ranging from ~ 0.02 M to ~ 0.3 M results in a significantly narrower linewidth of the indium¹¹⁵ resonance with increasing concentrations of the paramagnetic ion. Using an external reference of the indium solution without a paramagnetic ion, an attempt was made to measure the chemical shifts, called contact shifts, produced by introduction of the paramagnetic material. The observed resonance broadens with use of the reference, presumably because of a shift of the two indium signals from one another. It appears necessary to use a reference with a narrower linewidth, and a solution of In(III) in concentrated HCl, which presumably will have the more symmetrical species InCl_4^- , will be examined.

Gallium(III) studies in HCl have been started. Approximately 1 g Ga_2O_3 was dissolved in 6 M HCl. The resonance spectrum of gallium⁷¹ was measured at 12.984 Mc at a field of 10 KG. Two lines were present, the upfield, narrower of the two having a linewidth of ~ 500 cps. A solution more concentrated in HCl was made, and the linewidth was reduced to 113 cps. However, the intensity of the signal was low, and a third solution was made, approximately doubling the indium concentration. Experiments will now be performed to observe changes in linewidth and shift with the addition of paramagnetic ions. Measurements at different temperatures will be required to interpret the line broadening data.

RADIATION EFFECTS ON METALS - T. K. Bierlein

This program is directed toward (1) establishing the combined effect of impurities and neutron irradiation on the properties and structure of specific metals, and (2) deducing from thermally activated recovery processes how the damage state can be altered. Polycrystalline specimens of molybdenum, rhenium, and nickel were studied during the month.

The mechanism by which defect clusters are annealed out in high purity nickel is being examined in detail. Specimens irradiated to 5×10^{18} nvt have been annealed for 4, 6, and 24 hours at 450°C. Electron microscope observations show that there is little change in the density and size distribution of defect clusters between the 4 and 6 hour annealing times. After the longer 24 hour annealing treatment the density of defect clusters was reduced by a factor of 3 and their average size increased. Specimens are currently being annealed for 96 hours and will be examined in the hope that an activation energy for the annealing process can be established. Nickel specimens irradiated to 1×10^{19} and annealed at 450 and 500°C for 6 hours behave in a manner essentially identical to those irradiated to a lower exposure. The number of clusters and loops are reduced and their size increases upon annealing. Apparently, dislocation loops have not interacted because of the small number of defects present in the as-irradiated state.

Analysis of the diffraction patterns of the irradiated nickel foils has been facilitated by incorporating conclusions from a comprehensive treatment of diffraction effects from stacking faults. As reported earlier, shifts of the X-ray peaks were observed for irradiated nickel in the as-irradiated condition while the patterns were normal after annealing. The peak shifts were in the opposite sense from those predicted by theories of stacking faults. However, the more comprehensive treatment showed that peak shifts for extrinsic and intrinsic faults should be opposite in sense.

The shifts observed in the irradiated nickel samples are in the direction predicted for extrinsic stacking faults. Extrinsic faults are those formed by the insertion of an extra layer in the stacking sequence, as would result from an agglomeration of interstitial atoms.

Foil specimens of high purity molybdenum and rhenium have been recovered from a capsule after irradiation to a nominal exposure of 2.5×10^{19} nvt at a temperature of 500°C. Examination of the molybdenum

specimens discloses the presence of dislocation loops having diameters up to 300Å and a density of approximately $10^{15}/\text{cm}^3$. This is in marked contrast to observations made on samples irradiated at 40°C where a high density of small clusters are observed. The crystallography and character of these large loops are now being studied.

The molybdenum foil irradiated at 500°C has been examined by X-ray diffraction. No line broadening or lattice parameter changes were observed. Preliminary small-angle-scattering experiments indicate an appreciable scattering effect which is tentatively ascribed to scattering centers of about 150Å in diameter, if spherical.

A preliminary evaluation of activation volume measurements for molybdenum samples irradiated to 5×10^{18} nvt in the (1) irradiated, (2) post-irradiation annealed at 185°C, and (3) post-irradiation annealed at 600°C conditions shows several significant features.

- a. The activation volume increased with irradiation as observed previously; however, the increase with exposure to 5×10^{18} nvt was somewhat greater than for samples irradiated to a lower exposure of 1×10^{18} nvt.
- b. The activation volume decreased after a 2-hour anneal at 185°C; however, the amount of recovery was less than for samples irradiated to 1×10^{18} nvt.
- c. The activation volume decreased further after a 2-hour anneal at 600°C. This anneal did not produce complete recovery, in contrast with previous observations for samples irradiated to 1×10^{18} nvt and 1×10^{17} nvt.

The purification of molybdenum in a ZrH_2 furnace system has not reached desired levels at temperatures to 1300°C. Therefore, a higher-capacity power supply is being employed to increase furnace temperature to 1500°C. The increased interstitial diffusion rates at these higher temperatures should increase the rates and extent of purification.

A system for adding controlled amounts of carbon to molybdenum is now in operation. The molybdenum is heated to very high temperatures while in contrast with $\text{H}_2\text{-CH}_4$ mixtures. An initial run has been carried out at 1800°C in which no serious operational difficulties occurred, and the samples are being analyzed.

Polycrystalline and single crystal tensile specimens of rhenium have been encapsulated for irradiation. Goal exposures are 1×10^{18} and 7×10^{18} nvt.

PLUTONIUM PHYSICAL METALLURGY RESEARCH - R. D. Nelson

The objective of this program is to obtain fundamental information on the structure, properties, and metallurgical behavior of high purity plutonium, plutonium alloys, and other transuranic elements. The current activities are: 1) Studying the deformation processes of alpha and beta plutonium, 2) investigating solid-state reactions in plutonium and plutonium alloys, and 3) determining the properties of alpha and beta plutonium as a function of prior thermal and mechanical treatment.

A sufficient quantity of high precision electrical resistivity data has been analyzed to verify the very real and consistent difference in the resistivity of beta-phase plutonium formed from the alpha phase as compared with that formed from gamma. These data, together with the large difference in mechanical properties and the crystallographic differences indicated by x-ray diffraction, suggest strongly that another phase (perhaps metastable) exists in plutonium. Experiments on the stress dependency of creep of the two types of beta plutonium were completed. They revealed that the activation energy (Q_c) for creep of beta formed from gamma was independent of applied stress but that the activation energy for creep of beta formed from alpha was stress dependent. More specifically, for beta formed from gamma $Q_c = 26 \pm 1$ kcal/g-atom at all stresses between 3000 psi and 10,000 psi, but for beta formed from alpha Q_c decreased from 40 ± 2 kcal/g-atom at 1000 psi to 18 ± 2 kcal/g-atom at 7500 psi.

Resistivity and x-ray diffraction data indicate that cycling through the beta-gamma-beta transformations tends to suppress the formation of this suggested additional phase. But mechanical property data show that the high ductility and relatively low strength of beta cannot be restored by a second excursion into the gamma region. The significance of this finding is still under consideration.

STATISTICAL EVALUATION AND DEVELOPMENT - C. A. Bennett

Work continued on the designation of a Fortran II language version of the PEAK program for locating total absorption photo peaks in a gamma ray spectrum. The first draft of the mathematics of the program was completed and is in the process of being revised for inclusion with a description of the program as a formal Battelle-Northwest report.

A number of test cases were run on the Univac 1107 and IBM 7090 versions of the GEM program to check out the compatibility of the two programs.

A stochastic model was constructed to simulate the randomness in a recorded mass spectrometer spectrum in order to investigate the precision of isotopic ratio estimates as a function of the counting schedule. A formula was devised for the spectrum counting schedule for the several isotopic peaks of an elemental spectrum which maximizes either the precision of an individual ratio or the sum of the variances of all the ratios in the spectrum.

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