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HYDROLYSIS OF PLUTONIUM: CORROSION KINETICS IN DMSO SOLUTIONS CONTAINING SIMULATED HIGH EXPLOSIVE AND WATER

by

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ABSTRACT

A sequence of experiments is described that address the compatibility of plutonium metal with dimethyl sulfoxide solvent and with solutions containing simulated HMX explosive and simulated explosive plus water. In the absence of water, reaction is slow and forms a thin adherent product layer on clean metal surfaces. Corrosion of oxide-coated plutonium is observed after 15 to 20 days in a solution containing 0.18 mass % (0.11 M) water. After corrosion initiates, the rate accelerates rapidly and attains a value of 0.13 mg Pu/cm^2 h with a surface that is approximately one percent active. Dependence of the Pu+H_2O reaction on water concentration is evaluated using the data from literature sources. Hazards associated with the use of wet dimethyl sulfoxide as a solvent for removing explosives during weapon dismantlement are identified and a simple method for their mitigation is outlined.

INTRODUCTION

A procedure that employs dimethyl sulfoxide (DMSO) as a solvent has been developed for removing plastic-bonded HMX explosives from nuclear assemblies during weapon dismantlement.[1] As noted by Colmenares and LeMay in a recent report on work that parallels and complements this study, [2] a finite possibility exists that DMSO solutions containing HMX may come in extended contact with plutonium. Concerns arise because DMSO is an extremely hygroscopic compound[3,4] and liquid water is known to readily corrode plutonium metal with formation of oxide hydride powder plus hydrogen.[5,6] Concerns also arise in the case of a prolonged exposure period because radiolytic processes may generate additional water and other corrosive species as well as non-condensable gases over time.

The potential hazards posed by the combined chemical and radiolytic system are sufficient to warrant investigation of the compatibility between plutonium and solutions of DMSO containing HMX and water. Since safety and security restrictions exclude explosive materials from the plutonium facility at Los Alamos, corrosion tests were conducted using a non-explosive chemical substitute for HMX.

EXPERIMENTAL

The compatibility of plutonium with DMSO and selected DMSO solutions in air was investigated by a sequence of tests with a single sample of delta-phase plutonium alloy. The Pu test specimen (mass = 8.91 g, geometric surface area = 8.4 cm^2) was sheared from a sheet of weapons grade metal. Freshly cut edges and unaltered faces of the sample allowed the corrosion behavior of clean and oxidized surfaces to be investigated simultaneously. The metal sample was placed in a borosilicate glass container fitted with a ground-glass closure that prevented loss of solvent and absorption of atmospheric moisture. Different test conditions were established by sequentially adding solutes to an initial DMSO charge of 50 ml. DADN, the trans-diacetyl dinitro compound in which two of the nitro groups on the HMX ring are replaced by acetyl groups, was used as a substitute for high explosive.

Three compatibility tests were performed in sequence using pure DMSO, a DMSO+DADN solution and a DMSO+DADN+H_2O solution. The Pu sample was submerged in DMSO, periodically examined for evidence of corrosion and weighed at the end of the eight-day test period. The condition of the sample was monitored for an additional eight days after 21 g of DADN was combined with the solvent. Since the DADN formed a thick gelatinous mixture, inspection required that the sample be removed from the test medium for a brief period. A quantity of water (0.10 g) was subsequently added to achieve an H_2O concentration of 0.11 M (0.18 mass %) and the corrosion behavior was monitored by visual and gravimetric methods for a final period of 38 days. Photographs of the sample were obtained at several points during the combined test period of 54 days.

The average corrosion rate was determined from the mass loss observed during the final 11 days of the test. The total mass change was measured after the plutonium sample had been rinsed with DMSO and all loose corrosion product had been removed from the surface.

RESULTS

As anticipated, corrosion of plutonium metal was very slow in the absence of water. No measurable change in sample mass was observed after the eight-day exposure to DMSO. Whereas the oxidized surfaces of the sample appeared unaltered, the freshly cut edges acquired a deep blue color indicating that a thin adherent layer of corrosion product had formed. Likewise, no significant change was seen after addition of DADN; however, the color of the edges turned brown suggesting that a somewhat thicker product layer had formed during the eight-day test period.

The behavior observed after addition of water suggests a nucleation period followed by accelerating corrosion. No change in mass or appearance of the sample was detected after five days. After an additional 22 days, a mass loss of 0.01 g was measured and several extremely small black spots were found on the oxidized surface of the sample. An additional mass loss of 0.30 g occurred during the final 11 days of the test. Black corrosion spots were evident on the upper oxidized surface and on an edge where a thin burr of metal had been left by the shearing operation. Less than five percent of the surface was covered by corrosion distributed over a range of spot sizes that varied from a large site with a diameter of several millimeters to numerous extremely small sites. In some areas, corrosion appeared to be concentrated along scratch marks on the sample surface. A somewhat surprising observation is that corrosion sites appear only on the upper surface and one edge of the sample; sites were not evident on the surface facing the bottom of the test vessel.

The average corrosion rate determined for the final eleven-day period is 0.13 mg Pu/cm^2 h. This value is based on the total geometric surface area of the sample.

DISCUSSION

The sequence of tests performed in this study suggests that water-induced corrosion of plutonium is the most significant process occurring in a DMSO+HMX system. Corrosion involving dry solvent or dry solutions of HMX and radiolytic processes are apparently slow compared to hydrolysis of the metal.

The corrosion process occurring in wet DMSO is apparently similar to the reaction observed in water and aqueous solutions.[5,6] For the reaction in aqueous media, quantitative PVT (pressure-volume-temperature) data, X-ray diffraction measurements and chemical analyses show that the black corrosion product is PuOH, the monoxide nonohydride of Pu(III). The corrosion reaction is described by Equation 1.

$$Pu\ (s) + H_2O\ (l) \longrightarrow PuOH\ (s) + 1/2\ H_2\ (g). \qquad (1)$$

The oxide hydride product is a fine powder (66 Å average particle size from X-ray data)[5] identified as the source pyrophoric behavior in process operations at the Rocky Flats Plant.[7] Equation 1 is the first in a sequence of eight consecutive reactions that progressively generate hydrogen and ultimately form PuO_2. The rate of $Pu+H_2O$ corrosion is strongly dependent on pH and on the ionic (salt) concentration of the aqueous solution.

The rate of corrosion of plutonium by water in DMSO is expected to depend on several parameters, including water concentration, acidity, salt concentration and time. However, pH and ionic strength are not readily defined for DMSO, a non-aqueous and aprotic solvent. Onset of the reaction should depend on the surface condition of the metal. For gas-solid processes, the initial reactivity of the solid surface is indicated by the time dependence of the rate.[8] If reaction nucleates at isolated sites, the corrosion rate typically rises exponentially with time as sites grow and their numbers increase. If the entire surface is active initially, the rate normally decreases as the product layer becomes thicker over time.

Comparison of the average corrosion rate measured in this study with results from other work reveals several unanticipated findings. As shown by data in Table I, the corrosion rate of plutonium in water is increased by a factor of more than 10^4 when salts (e.g., NaCl or $CaCl_2$) are added to form 1 M solutions. Because of the comparatively low water concentration and the absence of salt-like materials in the present study, one might expect to observe a corrosion rate similar to that for deionized water. However, the experimental value is only a factor of 10 to 100 less than that for 1 M salt solutions.

Unanticipated kinetic behavior is also evident when the corrosion results are compared with the value derived from parallel experiments performed at Lawrence Livermore National Laboratory.[2] The rate result presented in Table I is an average derived from the mass loss percentages (3.2 and 4.2 mass %) reported for two tests with DMSO+HMX solutions containing 2.0 % water ($[H_2O] = 1.2$ M). Since neither the masses nor the geometric surface areas of the test specimens are reported, the surface area to mass ratio has been bracketed by calculating values for a range of Pu test mass in limiting geometries. For a 10 g mass in spherical and in 1.0 mm-thick square geometries, the area:mass ratios are 0.35 and 1.3 cm^2/g, respectively. Such values are surprisingly insensitive to mass; e.g., ratios for 1 g and 100 g samples differ by a factor of five for spheres and by only 20% for 1.0 mm-thick squares. The median value of 0.8 cm^2/g for a typical 10 g laboratory test specimen has been adopted for the rate calculation and a time period of 400 h has been used because significant reaction was not observed during the initial 100 h of the 504 h test. The reported uncertainty in the average rate (0.12 ± 0.0.08 mg Pu/cm^2 h) reflects the difference in mass loss percentage of the two experiments. Although the H_2O concentration was ten times greater than that of this work, the average corrosion rates obtained from the two studies are identical.

Dependence of the corrosion rate on water concentration is complex and cannot be fully interpreted. A concentration dependence for corrosion is evidenced by the absence of corrosion in dry DMSO and by the lack of detectable reaction on the bottom of the plutonium sample in this study. The absence of corrosion sites on the lower surface is attributed to slow transport of water from the bulk solution into the thin solvent layer between the sample and the container. However, coincidence of the rates at water concentrations differing by a factor of ten suggests that both conditions are in a regime where $[H_2O]$ is not the rate-determining parameter. This conclusion is supported by applying a surface area correction to the measured value from our study and comparing the result with the range of corrosion rates observed in tests with 1.0 M salt solutions and fully active surfaces. Since one percent or less of the total plutonium surface was active at the midpoint of the test period in the present study, the average corrosion rate for a fully active surface in wet DMSO is expected to equal or exceed 13 mg Pu/cm^2 h, a value well within the range listed in Table I for salt solutions having $[H_2O] = 55.5$ M. These observations suggest that the region of kinetic dependence on $[H_2O]$ appears in the range below 0.1 M.

As observed in prior studies of the $Pu+H_2O$ reaction,[5,6] corrosion of plutonium by water in DMSO is apparently independent of alloying. Unalloyed (α-phase) metal is frequently more reactive than δ-phase alloys, but the rate data in Table I suggest that this is not the case for corrosion by aqueous media or by wet DMSO+HMX solutions.

Analyses of the gaseous products formed during tests with dry and wet DMSO solutions of HMX,[2] indicate that radiolytic processes are also altered by the presence of water. Whereas the major gases observed by Colmenares and LeMay with dry solvent were N_2, N_2O and NO, comparatively large amounts of H_2 and N_2O were formed with wet solutions. Perhaps the most surprising result of both tests with water is that the amount of dinitrogen monoxide observed is approximately a factor of two greater than the amount of hydrogen. Although the true ratio of these products was altered by reaction of H_2 with unsubmerged portions of the plutonium samples, formation of N_2O appears to be markedly enhanced by the presence of water. One direct route to this species involves cleavage of two nitrogen-carbon bonds in the HMX ring and loss of an oxygen from the nitro group, but a simple mechanism is not apparent for such a process or for the apparent promotion of radiolytic decomposition by water.

The possibilities of enhanced corrosion and radiolysis are compounded by the rate of water adsorption by DMSO.[4] The rate of water adsorption from air depends on relative humidity (RH) and extent of saturation as well as solvent surface area. At 22 °C and RH values of 32 and 92%, initial adsorption rates are approximately 0.04 and 0.2 mass % per hour, respectively, with solvent surface areas of about 2.5 $cm^2/100$ g DMSO. At 32 % RH, the solution reaches saturation (approximately 23 mass % H_2O) after about 30 days. The initial water adsorption rate, R, is closely approximated by a linear function of the humidity: $R = 0.036$ (% RH). The rate of water adsorption by a surface layer of DMSO in 32% RH air (1.1 mg/cm^2 h) equals the maximum anticipated rate of water consumption (1.0 mg/cm^2 h) based on Equation 1 and the estimated rate (13 mg Pu/cm^2 h) for a totally active Pu surface. In addition to increasing the corrosive capacity of DMSO solutions, adsorption of atmospheric moisture may also increase the corrosion rate.

Definition of the potential consequences of plutonium corrosion by water is instructive. The rate for a totally active plutonium surface corresponds to the loss of 8.2×10^{-4} cm Pu/h. If corrosion occurs at this rate on both surfaces of the metal and is not limited by the availability of water, a 2-mm-thick piece of metal will be consumed in about five days.

CONCLUSIONS

In combination with data from other sources, our measurements show that plutonium corrodes at a rate equivalent to that encountered with sea water and aqueous salt solutions, if the water concentration in the DMSO exceeds 0.1 M (0.18 mass %). This result is particularly relevant to the removal of HMX from weapon components because the recommended acceptance criteria for DMSO at Pantex allows up to 1% (0.56 M) H_2O[1] and because additional moisture may be absorbed from the atmosphere.

Several potential hazards are associated with $Pu+H_2O$ corrosion. As noted above, the oxide hydride product is a fine pyrophoric powder. In two instances at Rocky Flats, hydrogen formed by water corrosion of plutonium in sealed plastic bags apparently ignited when the bagging failed and the oxide hydride spontaneously reacted with air.[7] Particle size data for the oxide hydride[5] and the similar size distribution anticipated for oxide formed by exposing PuOH to air suggest that all particles from the $Pu+H_2O$ reaction are in the respirable range with geometric diameters ≤ 3 μm.

The potential consequences of DMSO radiolysis also merit comment. The formation of explosive and non-condensable gases presents obvious hazards. However, analyses of the gases formed during exposure of DMSO+HMX solutions to plutonium show that small quantities of NO_2 appear in the product.[2] Dinitrogen tetroxide, the dimeric species existing in equilibrium with NO_2, is identified in material safety data information as incompatible with DMSO because of the potential for "violent or explosive reaction."[9]

These observations suggest that prolonged exposure of plutonium to DMSO+HMX solutions is not advisable. In this study, corrosion of oxide-coated metal nucleated after a period of 15 to 20 days (420 ± 60 h), is a substantially longer period than the 100 h induction time observed in tests with burnished metal surfaces.[2] On the basis of their results, Colmenares and LaMay recommend that DMSO solutions not remain in contact with Pu for more than 100 h. Even though the results for oxide-coated surfaces may be more representative of actual disassembly condition, a maximum exposure period of 4 to 5 days seems prudent.

Fortunately, the hazards presented by exposure of plutonium to DMSO solutions containing HMX and water can apparently be remedied using simple equipment and procedures. The vapor pressures of DMSO and water are sufficiently high that both species may be removed and separated from non-volatiles under dynamic vacuum at room or component temperatures. [10] Vacuum drying procedures have been used effectively to remove water from the oxide hydride corrosion product.[5] In addition to a commercial vacuum pump or other vacuum source with an ultimate capability of 0.01 torr or less, equipment requirements include an evacuable chamber with dimensions large enough to accommodate any plutonium-containing component, with a sealable closure and a leak rate less than 10^{-4} std cm^3/s, with a sensitive absolute pressure gauge and with tabulation incorporating in-line metallic particle filters and valves. Additional filters and cryogenic traps to collect all materials coming from the chamber and a source of argon or other inert gas might be placed in a manifold between the chamber and pump. This equipment should be in place and ready for service at all times.

The response to an incident in which DMSO solution contacts plutonium should be facile and rapid if equipment is available. After placement in the chamber (either directly with an unsealed plastic or metallic foil covering), the component would be exposed to a dynamic vacuum for a period of time necessary to remove major fractions of DMSO and water. Progress of the separation process could be monitored by periodically comparing static chamber pressure with equilibrium vapor pressures for DMSO+PBX-9404 (LX-10) could be stored in the chamber under vacuum or inert gas and the chamber pressure could be continuously monitored or adjusted until plans for addressing the situation are developed and implemented. Although an assessment of the hazards associated with HMX residues from DMSO solutions shows that they "are not significantly more sensitive than the base explosives," [11] possible effects of extended alpha-radiation exposure on HMX residues might also be considered.

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Table I. Kinetic Data for Corrosion of Plutonium and Delta-Phase Alloy in Media with Different Concentrations of Water

Metal Phase	Medium	H_2O Conc. (moles/ liter)	Rate (mg Pu/cm^2 h)	Reference
α	deionized H_2O	55.5	6×10^{-5}	5
α and δ	1 M aqueous salt	55.5	2.4-186[a]	5
α	DMSO+HMX	1.23	0.12±0.08[b]	2
δ	DMSO+DADN	0.11	0.13	this work

a. Corrosion rates varied over a range depending on the anion and the cation of the salt.

b. Rate data were derived from information in Reference 2 by procedures outlined in the text.

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