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ABSTRACT

Characterization of glovebox atmospheres and the black reaction product formed on plutonium surfaces shows that the abnormally rapid corrosion of components in the fabrication line is consistent with a complex salt-catalyzed reaction involving gaseous hydrogen chloride (HCl) and water. Analytical data verify that chlorocarbon and HCl vapors are present in stagnant glovebox atmospheres. Hydrogen chloride concentrations approach 7 ppm at some locations in the glovebox line. The black corrosion product is identified as plutonium monoxide monohydride (PuOH), a product formed by hydrolysis of plutonium in liquid water and salt solutions at room temperature. Plutonium trichloride ($PuCl_3$) produced by reaction of HCl at the metal surface is deliquescent and apparently forms a highly concentrated salt solution by absorbing moisture from the glovebox atmosphere. Rapid corrosion is attributed to the ensuing salt-catalyzed reaction between plutonium and water. Experimental results are discussed, possible involvement of hydrogen fluoride (HF) is examined, and methods of corrective action are presented in this report.

Introduction

The existence of an abnormally corrosive environment in the fabrication glovebox line at the Los Alamos Plutonium Facility (TA-55) is shown by recent observations of the rates at which surfaces of delta-phase plutonium alloy tarnish and degrade. Unusual behavior became evident in the fall of 1997 during preparation of plutonium for process development. The surface of an alloy casting was abraded to remove a thick layer of black corrosion product that had formed during storage in an argon-filled glovebox. Mass measurements indicated that the extent of corrosion was five to ten times greater than expected for normal oxidation. The casting remained overnight in a lathe within the argon-filled glovebox. The next morning, surfaces of the casting were again heavily tarnished and black. When the casting was removed from the lathe, black corrosion product was found only on surfaces directly exposed to the glovebox atmosphere. Surfaces that had been masked by the vacuum chuck and tailstock support were untarnished. The casting was placed in a storage cooler at −20°C to retard further corrosion. During storage, the extent of corrosion continued to increase in unmasked areas, while masked areas remained untarnished.

The observed corrosion behavior is inconsistent with the known reaction kinetic of the delta-phase alloy [1]. The glovebox in question was considered an inert environment because its argon atmosphere was protected from atmospheric contamination by an airlock for egress and by a continuous purge of argon through an exit bubbler. The argon atmosphere in the glovebox was certainly expected to be less corrosive than air. Kinetic results for the delta-phase alloy suggest that more than a month is required to form a blue (0.08 μm-thick) oxide layer in dry air at 35°C [1]. In order to form a blue layer within a matter of hours in air at this temperature, the humidity must approach the saturation pressure of 24 torr (31 570 ppm).

Additional observations verify that abnormally corrosive conditions exist in the argon-filled glovebox. In one case, alloy samples were cut and abraded for use in semiquantitative tests to assess the compatibility of metal with glovebox atmospheres at several locations in the line. The specimens were burnished to obtain clean metal surfaces, wrapped in foil, and enclosed in a plastic container. After overnight storage, the samples were so extensively tarnished that they were not usable for tests to estimate corrosion rates from interference color changes [1]. In addition, formation of black corrosion product on components in the glovebox is documented photographically [2]. The characteristic amber to brown oxide seen in photographs of a plutonium surface immediately after removing the metal from a sealed storage container was replaced by a black layer after several months of exposure to the glovebox atmosphere. Surfaces of the black product became green after extended exposure to the glovebox atmosphere.

Unexpected behavior was also encountered when corroded castings were burnished and used in process development tests. The surfaces of welds obtained with test specimens of abraded alloy appeared porous and spongy [2]. Methane (CH_4), ethane (C_2H_6) and small amounts of hydrogen (H_2) were found in the containment vessels after samples of abraded metal had been thermally processed at 400–500°C [3].

Photomicrographs of burnished alloy surfaces like those used in these tests show that islands of black corrosion product remained after abrasion [2], suggesting that corrosion proceeded by a pitting attack unlike the even advance of oxygen corrosion.

Efforts were initiated to define the source and chemistry of the abnormal corrosion reaction. Attention immediately focused on possible gas-phase contaminants because only unmasked areas of the abraded component were corroded. This report outlines the background information on which the investigation is based, describes hypotheses and experimental observations, defines the proposed corrosion process, and recommends possible corrective actions.

Background Information

A similar corrosion problem was encountered at the Rocky Flats Plant during the mid-1980s. Driers for air entering the building and the nitrogen-purge system for the gloveboxes were shut down for facility maintenance during the end-of-year break. Undried air flowed through the glovebox lines for more than a week. Two anomalies were observed after resumption of normal activities. Large black spots began to appear on the surfaces of in-process plutonium in patterns corresponding to hand prints that would result from normal handling. In addition, a sticky, viscous liquid was present on the surfaces of all galvanized hardware (pipes, conduit, electrical covers) inside the glovebox line. In some cases puddles of the substance had collected beneath galvanized objects. Further inspection showed that the sticky material was present on gloves in areas where components were normally handled. A correlation between this substance and the appearance of black spots was assumed.

Characterization of the sticky material helped to establish its chemical origin and properties. Chemical analysis showed that the substance was a highly concentrated zinc chloride ($ZnCl_2$) solution. The largest sources of chlorine in the fabrication facility were carbon tetrachloride (CCl_4), used as the solvent for oil in the machining area and 1,1,1-trichloroethane ($Cl_3C\text{-}CH_3$), used as the solvent for final cleaning of components. Chlorocarbons hydrolyze in air to form gaseous hydrogen chloride (HCl), a species that undoubtedly existed at low concentrations in the glovebox atmospheres. In all likelihood, HCl was also formed by radiolytic elimination from trichloroethane or by radiolytic polymerization of chlorocarbon solvents with oils or other hydrocarbons. Over a period of many years, zinc (Zn) in the galvanized coatings reacted with the HCl to form $ZnCl_2$, a deliquescent material that is gradually dissolved and liquefied by absorption of moisture from air. Exposure to high moisture levels during the shutdown caused the accumulated product to be transformed into a concentrated zinc chloride solution.

The proposed sequence of reactions for the formation of zinc chloride solution in the chemical and radiolytic environment of the glovebox line is

$$Cl_3C\text{-}CH_3\ (g,\ l)\ \text{(alpha particle)} \dashrightarrow Cl_2C{=}CH_2\ (g,\ l) + HCl\ (g), \qquad (1)$$

$$C\text{-}Cl\ (l,\ s) + C\text{-}H\ (l,\ s)\ \text{(alpha particle)} \dashrightarrow C\text{-}C\ (l,\ s) + HCl\ (g), \qquad (2)$$

$$C\text{-}Cl\ (l,\ s) + H_2O\ (ads) \dashrightarrow C\text{-}OH + HCl\ (g), \qquad (3)$$

$$Zn\ (s) + 2\ HCl\ (g) \dashrightarrow ZnCl_2\ (s) + H_2\ (g),\ \text{and} \qquad (4)$$

$$ZnCl_2\ (s) + x\ H_2O\ (g) \dashrightarrow ZnCl_2\ (aq\ soln)\ . \qquad (5)$$

In these equations, gases, liquids, solids, adsorbed species, and aqueous solutions are indicated by g, l, s, ads, and aq soln, respectively. Radiolytic reactions are identified by the presence of an alpha particle, which releases 5 MeV of energy per decay of a ^{239}Pu isotope. Radiolytic reactions resulting in HCl formation by chemical elimination and polymerization reactions are shown by Equations (1) and (2), respectively. The identities of liquids and solids in Equations (2) and (3) are not specified because they represent a broad spectrum of condensed substances that might be polymerized on surfaces in the glovebox. The value of x in Equation (5) is unknown, but the amount of absorbed water required to form a thick liquid is probably on the order of 20 to 30 H_2O per $ZnCl_2$.

Corrosion apparently occurred at every location that the plutonium surface was contaminated by zinc chloride. The black product resembled that obtained from reaction of plutonium with liquid water [4,5,6]. The chemistry and the kinetics of plutonium corrosion are dramatically altered when the metal is submerged in water or salt solution. Although plutonium dioxide (PuO_2) is formed by reaction of metal with water vapor [8, 9], black plutonium monoxide monohydride (PuOH) is formed by corrosion of Pu submerged in liquid water at room temperature. The rate of aqueous corrosion is sharply increased by adding soluble salts to the water. Plutonium surfaces contaminated by $ZnCl_2$ behaved in a similar manner, suggesting that the observed corrosion resulted from salt-catalyzed reaction of water to form PuOH.

Formation of plutonium monoxide monohydride in near-neutral water is described by the following equation [4,5,6]:

$$Pu\ (s) + H_2O\ (l) \dashrightarrow PuOH + 1/2\ H_2\ (g)\ . \qquad (6)$$

As the reaction proceeds, the oxide hydride spalls from the metal surface as a fine black powder that exhibits pyrophoric tendencies when dry. The composition of the product was determined from experimental data showing that 0.5 mol of H_2 is formed by the reaction of 1.0 mol of Pu. X-Ray diffraction results show that the product has a face-centered cubic lattice ($a_0 = 5.400 \pm 0.003$ Å, theoretical density = 10.80 g/cm^3) consistent with a CaF_2-related structure formed by a cationic sublattice of Pu(III) and an anionic sublattice of O^{2-} and H^-. Microbalance and mass spectrometric data show that dry PuOH decomposes with evolution of H_2 when heated in vacuum at 105 to 195°C. The mass loss (0.41 ± 0.02 mass %) observed during decomposition is in close agreement with the theoretical value of 0.39 mass % for PuOH. Spectroscopic data and the absence of additional mass loss upon continued heating of the product in vacuum to 500°C show that the black product is not hydroxide. Identification of the oxide hydride solely from diffraction data is complicated by the similarity of its structure and lattice parameter to those of CaF_2-type PuO_2 (a_o = 5.397 Å) and PuH_2 (a_o = 5.359 Å). Extensive experimental studies demonstrate that the corrosion product is not a mixture of dioxide and dihydride [4].

Although independent of alloying, the rate of plutonium corrosion according to Equation (6) is markedly enhanced by the presence of soluble salts (e. g., chlorides, bromides, nitrates) in the aqueous phase [6]. In near-neutral ($5 < pH < 8$) solutions, the corrosion rate (R) is insensitive to alloying, rapidly enters a linear (constant rate) stage of corrosion, and is an exponential function of the molar salt concentration ([salt]). The dependence of R on [salt] during the linear stage of reaction is shown in Figure 1 and is described by

$$R \text{ (in mg Pu/cm}^2\text{ hr)} = 7.25\,[\text{salt}]^{0.43}\ . \qquad (7)$$

R in tap water containing 23 ppm (0.0013 M) soluble salts is almost a hundred fold faster than the corrosion rate in distilled water. Increasing the salt concentration to 1.0 M (17 850 ppm) causes an additional ten-fold increase in the corrosion rate of water. The corrosion rate is not significantly altered by the identities of dissolved cations or anions. Analytical data show that salt species are not incorporated in the solid product; they only catalyze corrosion of Pu according to Equation (6).

Observed changes in corrosion rate at surface locations contaminated with zinc chloride are consistent with the effect of salt concentration on R. If the sticky material formed by exposing zinc chloride to moisture had 30 H_2O for each $ZnCl_2$, the salt concentration was 1.8 M. The linear corrosion rates for alloyed and unalloyed plutonium in salt solution at this concentration are expected to be about 10 mg Pu/cm^2 h [6], which corresponds to formation of a 10 µm thickness of PuOH per hour. In comparison, formation of a 1-µm-thick oxide layer on clean alloy in moisture-saturated air at 100% relative humidity takes approximately 40 days at 35°C [1]. The actual rates of corrosion in the glovebox lines at Rocky Flats were much less than expected for a salt solution with an unlimited supply of water and were probably determined by humidity and the collision frequency of water molecules with zinc chloride-contaminated surfaces.

The proposed process for salt-catalyzed corrosion by moisture was directly demonstrated by laboratory tests [8]. Small particles of reagent-grade, anhydrous $ZnCl_2$ were placed on the surfaces of oxide-coated alloy samples that were subsequently exposed to undried glovebox air. After a few hours, the salt particles were no longer visible and small black corrosion spots had appeared. After several days, the spots were noticeably larger and spallation of black product was evident.

Corrective actions were taken and the effects of isolated black spots on the components were evaluated. Formation of spots on new components was eliminated by cleaning all zinc chloride from glovebox lines, replacing all gloves, and reactivating driers for incoming air. Acceptance criteria for components with spots were established after tests had been performed to assess their effect on specifications. Although the quantities of oxide hydride were small and did not present a pyrophoricity hazard, hydrogen-air mixtures formed by corrosion of site-return components after leaching in aqueous acid were reactive [9]. Recent tests with PuOH-coated specimens show that the hydride-catalyzed reaction of plutonium with air [10] occurs if the oxide hydride is thoroughly dried and rapidly exposed to air [11].

Hypotheses to Explain Recent Observations

The nature of the corrosive environment in argon-filled atmosphere gloveboxes is elucidated by considering the observed behavior. Occurrence of corrosion only in unmasked areas of a component suggest that reaction is initiated by a gas-phase contaminant in the argon atmosphere. Continued corrosion in unmasked areas during low temperature storage in air suggests that further reaction on these surfaces is promoted by a catalytic process (i. e., the rate is enhanced without consuming the catalyst) involving a second gaseous reactant. This second gaseous reactant must be present in both the glovebox and the storage atmospheres. The absence of corrosion in masked areas of the same component suggests that the initial contaminant is present at a low concentration in the argon glovebox, that a threshold exposure to the contaminant is necessary to initiate catalytic activity, and that this contaminant is either not present or inactive in the storage atmosphere. Although the second reactant must be present in storage, it is not highly corrosive in the absence of a catalyst.

The preceding observations and rapid formation of a black product are consistent with salt-catalyzed corrosion of plutonium by water to form PuOH. If this premise is true, the second reactant is water vapor, a species that is undoubtedly present in both the glovebox and storage atmospheres. Although one might assume that the storage atmosphere is very dry because ice collects in the cooler at –20°C, its presence actually ensures that an ample supply of water is available at an equilibrium pressure of 0.78 torr (1300 ppm at 580 torr). Identification of the gas-phase contaminant that reacts with plutonium to form a deliquescent salt is more difficult, but essential for resolving the corrosion issue.

Hydrogen chloride is a likely gaseous contaminant for producing a deliquescent salt on plutonium surfaces. HCl produced by hydrolytic and radiolytic processes described in Equations (1-3) reacts with Pu to form a surface layer of plutonium trichloride ($PuCl_3$).

$$\mathrm{Pu\ (s) + 3\ HCl\ (g) \dashrightarrow PuCl_3\ (s) + 3/2\ H_2\ (g)}\ . \qquad (8)$$

Like $ZnCl_2$, the trichloride is a deliquescent salt that hydrates, absorbs moisture, and forms a concentrated chloride solution capable of catalyzing aqueous corrosion of metal according to Equation (6) [12]. However, the plausibility of this process must be questioned because chlorine-containing solvents such as freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane, $Cl_2FCCClF_2$) have apparently not been used in the argon gloveboxes for several years. Although the argon flow used for purging gloveboxes is limited and inefficient, the presence of residual freon vapor seems unlikely. If present, chlorocarbon residues are most probably incorporated in polymerized deposits on glovebox surfaces.

Consideration must be given to a parallel process involving gaseous hydrogen fluoride (HF) instead of HCl. This possibility is supported by the presence of fluorine in freon 113 and in the perfluorocarbon replacement fluid (SF-2I) currently in use. Although fluorocarbons are inert and not readily hydrolyzed, radiolytic reactions provide a potential source of HF. Reaction of plutonium with hydrofluoric acid at low concentrations produces the trifluoride (PuF_3), but this product is insoluble in water and only slightly soluble in concentrated mineral acids [12]. Although formation of a salt solution suitable for catalyzing Equation (6) seems very unlikely, the observed corrosion might result solely from reaction of HF.

Experimental Methods

An experimental approach was developed to confirm or reject the hypotheses outlined above. These efforts focused on two areas: (1) specific verification of the presence or absence of HCl, HF, and potential sources for these species and (2) characterization of the black corrosion product. Additional corrosion possibilities would be considered only if neither hypothesis could be adequately confirmed.

Several methods were used to identify gas-phase constituents. The acidities of glovebox atmospheres were tested at selected locations in fabrication gloveboxes with pH indicator paper (Whatman Type CF, $0 < pH < 10$). Indicator tubes for specifically detecting and determining trace levels of HCl (Draeger, 1 to 10 ppm range) and HF (Draeger, 1.5 to 15 ppm range) were used to test glovebox atmospheres for these gases. A sample of the atmosphere in the Surveillance Glovebox was collected and analyzed by mass spectrometry (MS). Samples of the atmospheres in Surveillance and Bostomatic Gloveboxes were collected and analyzed by gas chromatographic-mass spectrometric (GC/MS) methods. Gaseous constituents separated on the basis of their chromatographic retention times were analyzed by mass spectrometry.

The black product formed on the plutonium surface was analyzed by X-ray diffraction (XRD) and by thermal-desorption mass spectrometry (TDMS). In the thermal desorption measurements, a sample of product-coated metal was heated at a constant rate in vacuum and the evolved gases were repeatedly analyzed as a function of temperature by MS.

Results and Discussion

The presence of acidic contaminants was indicated at several locations in the fabrication gloveboxes. Color changes of the indicator paper showed pH levels in the 0 to 3 range. It must be remembered that the indicator paper is intended for determining the pH of aqueous solutions and that the pH of a gas is meaningless. However, the presence of acidic species is consistent with a warning label recommending that the indicator paper not be stored in areas where acidic or basic fumes are present.

The presence of hydrogen chloride gas is shown by mass spectrometric analysis and Draeger tube indication. MS data for the gas sample from the Surveillance Glovebox show water and extremely small peaks at mass/charge ratios of 36 and 38 with relative intensities corresponding to the 3:1 isotopic ratio of ^{35}Cl to ^{37}Cl. The presence of HCl was verified by color indication of Draeger tubes with concentrations approaching 7 ppm at some locations.

Results of a survey to determine HCl concentrations in the glovebox lines are conveniently placed into three categories: (1) areas in which the presence of HCl was not detected, (2) areas in which moderate concentrations (0.5 to 1.0 ppm) of HCl were found, and (3) areas in which the highest concentrations (5 to 7 ppm) of HCl were present. HCl-free areas include dropboxes and connecting lines with high flow rates and frequent turnover of the air atmospheres. Moderate HCl levels were found in the Surveillance and Bostomatic Gloveboxes and in other argon-filled gloveboxes with limited turnover of the atmosphere. The highest levels were observed in storage coolers with essentially stagnant air atmospheres. The cooler used for storing the partially corroded component was periodically opened and had a moderate HCl level. Concentration gradients were observed within gloveboxes with the highest HCl levels near the bottom.

GC/MS analysis of gas samples from the Surveillance and Bostomatic Gloveboxes indicate the presence of chlorofluorocarbon vapors [13]. Two well-resolved peaks appear in the chromatograms for these samples. MS data identify the initial peak as freon 113. The second species is identified as 1,1,3,4-tetrachloro-1,2,2,3,4,4-hexafluorobutane ($Cl_2FC\text{-}CF_2\text{-}CClF\text{-}CClF_2$), a product that apparently results from radiolysis of freon 113 as follows:

$$2\ C_2Cl_3F_3\ (g) \dashrightarrow C_4Cl_4F_6\ (g) + 2\ Cl\ (g)\ . \qquad (9)$$

Atomic (free-radical) chlorine eliminated by this polymerization reaction is capable of extracting H from hydrocarbons, hydroxides, and other hydrogen sources to form HCl. The net process is similar to the reaction described by Equation (2).

Neither MS nor Draeger tube analysis of glovebox gases indicated the presence of hydrogen fluoride (HF), even though a fluorine source existed as chlorofluorocarbon vapor. This result suggests that elimination of F by a process like Equation (8) is unfavorable compared to that for Cl, or that the HF product has an extremely short life time. If hydrogen fluoride is formed by radiolysis of freon 113, dimers corresponding to elimination of two F ($C_4Cl_6F_4$) and one F plus one Cl ($C_4Cl_5F_5$) should be present in addition to that for elimination of two Cl ($C_4Cl_4F_6$). The absence of additional dimeric species indicates that HF is not formed and does not participate in the corrosion process.

As proposed by Sivils and Moy [13], radiolytic polymerization of freon 113 most likely proceeds via a free-radical mechanism. The suggested reaction path involves elimination of atomic chlorine from the $-CCl_2F$ moiety of freon 113 to form a specific free radical ($ClF_2C-CClF\cdot$). Association of two free radicals of this type produces 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane, a symmetric isomer of the proposed product (1,1,3,4-tetrachloro-1,2,2,3,4,4-hexafluorobutane). Appearance of this asymmetric isomer implies that free radicals are also formed by elimination of Cl from the $-CClF_2$ moiety. Therefore, a second symmetric isomer (1,1,4,4-tetrachloro-1,2,2,3,3,4-hexafluorobutane) is also expected to result from association of these free radicals. In all likelihood, the second GC peak is a mixture of three $C_4Cl_4F_6$ isomers formed by association of two free radicals, but the point cannot be adequately addressed by mass spectrometric analysis.

Results of XRD and TDMS data indicate that the black corrosion product is PuOH. Diffraction data for corroded surfaces show a fluorite-type fcc phase with a lattice parameter near that of dioxide, but a_0 cannot be defined with sufficient accuracy for distinguishing between PuO_2 and PuOH. TDMS data show that H_2, the only product of thermal decomposition, forms at 150 to 200°C. This decomposition range corresponds to that of PuOH [4], and is well below the 450°C temperature required to decompose PuH_2 at a measurable rate [14].

Thermal decomposition of residual PuOH provides a consistent explanation for unanticipated behavior encountered during attempts to use abraded metal for process development. Evolution of H_2 and formation of oxide residues during welding tests is consistent with observed weld porosity. Formation of methane and ethane during thermal processing is attributed to reaction of product hydrogen with carbon residues on surfaces within the containment vessel. In both instances, islands of PuOH apparently remained on the component surfaces after abrasion.

Continued reaction of the partially corroded component during low temperature storage is relevant to identification of the corrosion process. According to the proposed mechanism involving hydrogen chloride, $PuCl_3$ forms on exposed Pu surfaces in the HCl-contaminated glovebox atmosphere. Absorption of moisture by the deliquescent chloride product forms a concentrated salt solution on reacted metal surfaces. Salt-catalyzed corrosion proceeds with formation of black oxide hydride in these areas. Reaction continues as the chloride absorbs water in the relatively humid atmosphere of the cooler, but does not occur in untarnished areas of the component. This behavior seems somewhat inconsistent because HCl vapor was detected in the cooler and would be expected to form trichloride on untarnished areas during storage. The Pu+HCl reaction is strongly dependent on temperature [12] and the rate of $PuCl_3$ formation may be negligibly slow at −20°C and low HCl concentrations.

An additional point of uncertainty arises because measured humidity levels in the glovebox atmospheres are very low while rapid corrosion is observed. A direct relationship between humidity and corrosion rate is expected. Reported moisture levels in the fabrication lines range from 5 ppm in the argon-filled Surveillance Glovebox to 40 ppm in the air-filled trunk lines. As noted in the communication of these data [15] and in a memorandum of equilibrium water pressures of desiccants [16], these values are suspiciously low and calibration of the moisture analyzers must be questioned. The trunk-line value of 40 ppm is doubtful because ice collects in the coolers at -20°C. In order for ice to form and remain at this temperature, the H_2O concentration in the trunk line must consistently exceed 1300 ppm at 580 torr pressure.

An alternative source of HCl must also be considered because fabrication gloveboxes share an exhaust plenum with gloveboxes used for aqueous hydrochloric acid recovery. Countercurrent flow of HCl vapor into the fabrication line has been suggested. Differences in glovebox negativity undoubtedly exist within the system, but the average flow through each air-filled glovebox is 425 liter/min (15 cfm) and the cumulative flow rate within the plenum is so large that back-flow of gases is extremely unlikely. If HCl enters from the plenum, its concentrations should be highest in dropboxes and trunk lines and lowest in argon-filled gloveboxes and coolers that are physically isolated from the plenum system. The observed HCl distribution is the exact opposite of these expectations. Therefore, the possibility of deriving HCl contamination from other sources in the facility is extremely remote and does not merit further consideration.

Safety issues are raised by the observation of pyrophoric behavior for PuOH. Tests show that the oxide hydride is reactive [4,5,6] and that a surface layer of the product is capable of initiating the hydride-catalyzed reaction of plutonium with air [10]. Spontaneous ignition of plutonium is observed only if the product is prepared in liquid water, thoroughly dried in dynamic vacuum, and then rapidly exposed to air [11]. Pyrophoric behavior is not observed if dried oxide hydride is gradually exposed to air or if it results from salt-catalyzed corrosion by water vapor. After controlled exposure to air, the dried product could be handled in an air atmosphere and X-ray photoelectron spectroscopy (XPS) data show that the surface was covered by a layer of PuO_2 [4]. The green color that appeared on the product surface during exposure to glovebox atmospheres is characteristic of PuO_2 [12]. Slow formation of the dioxide layer apparently passivates the surface without generating heat at a rate necessary for spontaneous ignition. Although wet PuOH is not pyrophoric, H_2 is formed by a continuing series of reactions involving water [4, 5], and caution must be exercised to ensure that explosive mixtures do not form.

Conclusions

Experiments to characterize glovebox atmospheres and the black reaction product indicate that enhanced corrosion of plutonium in fabrication lines at TA-55 results from salt-catalyzed reaction of the metal by water. Data show that hydrogen chloride vapor is present in all gloveboxes in which plutonium surfaces rapidly tarnish. This highly corrosive species apparently reacts with plutonium to form a surface layer of trichloride. Deliquescence of that product forms a highly concentrated salt solution that catalyzes the reaction of plutonium with water. A chlorocarbon source of chlorine is identified and its radiolysis provides a direct route for forming hydrogen chloride. Properties of the black corrosion product are consistent with those of the monoxide monohydride formed by reaction of plutonium with water.

Definition of the corrosion process establishes its essential features and assists in identifying possible methods of remediation. Chlorine, hydrogen, and water are essential reactants and participate in gaseous forms. Corrosive conditions are promoted by a stagnant atmosphere. Possible corrective actions are based on reducing or eliminating reactive species from glovebox environments, on physically protecting plutonium from reactive vapors, and on increasing the turnover rates of stagnant atmospheres. Although advantage is gained by reducing the moisture concentration in glovebox atmospheres, elimination of that reactant is unlikely. The difficulty is compounded because moisture continues to react via the salt-catalyzed reaction after trichloride is formed, even though

HCl is no longer present. Prevention of the catalytic process is most likely achieved by eliminating all chlorine-containing vapors and residues from the glovebox environment.

Recommendations

The following are three possible methods for remediation of abnormally rapid corrosion of plutonium in the fabrication.

(1) Eliminate potential sources of chlorine. Use of freon 113 and other chlorocarbon solvents should be rigorously suspended and existing deposits of polymerized organic material and plutonium oxide particles should be removed from glovebox surfaces. Removal of sources for radiolytic chlorine (as well as bromine and iodine) is the only method with potential for preventing the catalytic reaction. Inorganic halides are of concern only if they are deliquescent.

(2) Minimize sources of moisture and hydrogen. Humidity and hydrocarbon residues should be maintained at the lowest possible levels to reduce the likelihood of HCl formation and to limit the rate and extent of corrosion by water. Accurate monitoring of humidity levels is essential for reliable process control and development of equilibrium standards is recommended for accurate calibration of moisture analyzers.

(3) Modify conditions and procedures to reduce the effects of reactive species. Possible changes include protecting components with aluminum foil wrap and/or closed storage containers, increasing the turnover rates of controlled-atmosphere gloveboxes, using in-line gettering techniques to reduce and control the concentrations of reactive species, and altering the atmospheric composition of gloveboxes to promote the formation of passive surface products. The formation of surface oxide in reduced-oxygen glovebox atmospheres at Rocky Flats apparently slowed the reaction of plutonium with of HCl vapor and storage of metal in a mildly oxidizing atmosphere is recommended.

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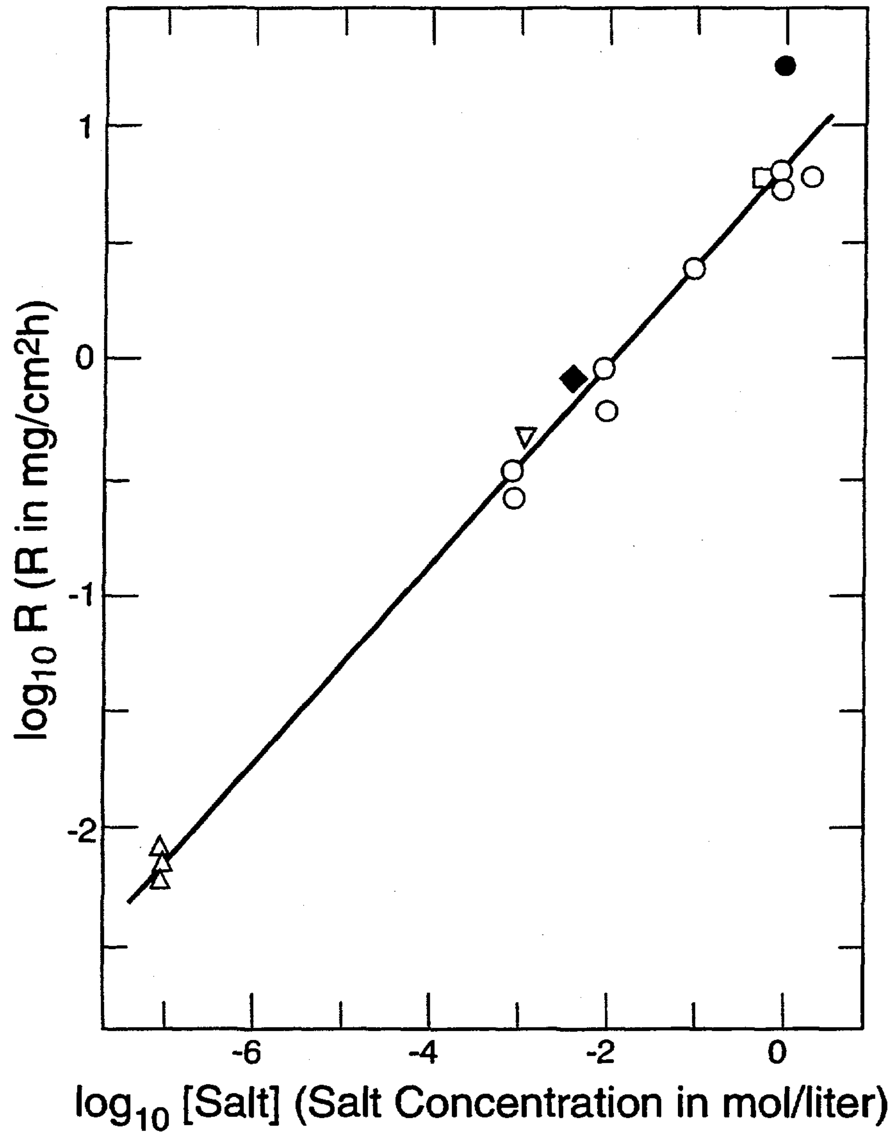

Figure 1. Dependence of the plutonium corrosion rate (R) on the molar salt concentration ([salt]) in aqueous solution at 25°C [6]. Rates for alpha- and delta-phase metals are indicated by filled and open symbols, respectively. Upright triangles, circles, the inverted triangle, the diamond, and the square are for distilled water, calcium chloride solutions, sodium chloride solution, and synthetic sea water, respectively.