THORIUM FLUORIDE REMOVAL FROM STAINLESS STEEL FOR A THIN FILM DEPOSITION CHAMBER RECYCLING

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ABSTRACT

Thorium fluoride, ThF_4, is currently the preferred low refractive index material, transparent from the UV to the IR, which is used in specialized optics. ThF4 is applied to transparent materials, such as glass and polycarbonate plastics to provide certain electrical and photon transmission properties. Common applications are for AR coatings in the 8 to 12 µm region; including high power CO_2 laser coatings and targeting optics for smart munitions. The ThF_4 is applied via a vacuum deposition process.

Vacuum deposition makes use of Thorium fluoride's sublimation at 800°C. E-beam or resistance-heated sources are used to heat the ThF_4 in a molybdenum or tantalum hearth. The recommended substrate (receiving the film) temperature is 175°C, inside a vacuum chamber with a pressure below 10^{-5} Torr. A typical chamber has dimensions of roughly 10' x 10' x 10', and contains various internal support structures and holding racks for receiving substrates. Material of construction is stainless steel. Evaporated films are very durable, chemically stable and exhibit low stress in thicknesses up to 2 µm. Essentially the coating cannot be removed from the target substrate. It is for this property and in spite of special precautionary measures needed with the use of ThF_4, that it is still the premier coating material for lasers in the 8-12 µm region.

However, in the process of coating the target substrate, the vacuum deposition process also coats the entire inside of the vacuum chamber with ThF_4. Thorium fluoride is a naturally radioactive material that must be handled and wastes disposed of in accordance with state and/or federal regulations. When a manufacturer wanted to make changes in the ownership of its existing chamber, it was also faced with a potentially significant disposal bill in order. By using the TechXtract® process to remove ThF4 from the chamber, the manufacturer reduced disposal costs, volumes, and was able to reuse the chamber.

INTRODUCTION

Thorium Fluoride Use and the Vacuum Metallization Process

The placement of thin films on a host substrate is a common industrial process with several variations. In a vacuum, gas pressure is less than the ambient atmospheric pressure. A plasma is a gaseous environment where there are enough ions and electrons for there to be appreciable electrical conductivity. Vacuum deposition is the deposition of a film or coating in a vacuum (or low-pressure plasma) environment. Generally, the term is applied to processes that deposit atoms or molecules one at a time, such as in physical vapor deposition (PVD) or low-pressure chemical vapor deposition (LPCVD) processes. It can also be applied to other deposition processes such as low-pressure plasma spraying (LPPS).

The vacuum in deposition processing increases the "mean free path" for collisions of atoms and high-energy ions and helps reduce gaseous contamination to an acceptable level. A minimum vacuum of below 10^{-5} Torr is required to create the a mean free path condition.

When establishing a plasma in a vacuum, the gas pressure plays an important role in the enthalpy, the density of charged and uncharged particles and the energy distribution of particles in the plasma. A plasma in a "good vacuum" provides a source of ions and electrons that may be accelerated to high energies in an electric field. Vacuum evaporation is used to form optical interference coatings using high and low index of refraction materials, mirror coatings, decorative coatings, permeation barrier films on flexible packaging materials, electrically conducting films and corrosion protective coatings. When depositing metals, vacuum evaporation is sometimes called vacuum metallization.

The deposition of Thorium Fluoride on glass is done to provide low index of refraction to optics which require high precision over great distances. The vacuum chamber required for the work is a highly machined precision piece of equipment. Military like tolerances are required in all parts specifications. Material of construction is stainless steel. Evaporated films are very durable, chemically stable and exhibit low stress in thicknesses up to 2 µm. Essentially the coating cannot be removed from the target substrate. It is for this property and in spite of special precautionary measures needed with the use of ThF_4, that it is still the premier coating material for lasers in the 8-12 µm region. These same qualities make removal of ThF4 from the chamber difficult.

Chemical and Physical Properties of Thorium

The physical and chemical properties of elemental thorium and a few representative water-soluble and insoluble thorium compounds are presented in Table 1. Water-soluble thorium compounds include the chloride, fluoride, nitrate, and sulfate salts (West 1983). These compounds dissolve fairly readily in water. Soluble thorium compounds, as a class, have greater bioavailability than the insoluble thorium compounds. Water insoluble thorium compounds include the dioxide, carbonate, hydroxide, oxalate, and phosphate salts. Thorium carbonate is soluble in concentrated sodium carbonate (West 1983). Thorium metal and several of its compounds are commercially available. No general specifications for commercially prepared thorium metal or compounds have been established. Manufactures prepare thorium products according to contractual specifications (Hedrick 1985)

Thorium is a metallic element of the actinide series. It exists in several isotopic forms. The isotope thorium-232 is a naturally occurring element that is radioactive. Ti decays through the emission of a series of alpha and beta particles, gamma radiation, and the formation of daughter products, finally yielding the stable isotope of lead, lead-208. The isotopes thorium-234 and thorium-230 are produced during the decay of naturally occurring uranium-238, the isotope thorium-228 during the decay of thorium-232, and the isotopes thorium-231 and thorium-227 during the decay of naturally occurring uranium-235. Of these naturally produced isotopes of thorium, only thorium-232, thorium-230, and thorium-228 have long enough half-lives to be environmentally significant. More than 99.99% of natural thorium is thorium-232; the rest is thorium-230 and thorium-228.

Including artificially produced isotope there are 12 isotopes of Thorium with atomic masses ranging from 223 to 234. All are radioactive and decay with the emission of alpha or beta particles and/or gamma radiation (West 1983). In general, the alpha particles are more intensely ionizing and less penetrating than the beta particles. The gamma radiation is the most penetrating of the three, but it has the least ionizing intensity. Alpha particles do not penetrate external skin to a sufficient depth to produce biological damage due to the protective effect of the epidermis. However, alpha particles emitted from thorium deposited

in the lung are able to penetrate lung tissue and produce adverse biological damage since the protective coating of the lung tissue is very thin. In turn, beta particles are able to penetrate the skin to a sufficient depth to cause biological effects in the skin just below the epidermis. Likewise, they penetrate lung tissues to a greater depth. Gamma rays can generally pass through all tissue and interact with tissue at any depth. Alpha particles give up all of their energy in a very short distance and, hence, produce ionization. Beta particles produce less dense ionization, and gamma rays produce less yet. In general, the severity of biological effects of exposures to ionizing radiations is proportional to the density of the ionization produced by their passage through tissue. Finely divided thorium metal is pyrophoric in air, and thorium ribbon burns in air to give the oxide. The metal also reacts vigorously with hydrogen, nitrogen, the halogens, and sulfur. Thorium compounds are stable in +4 oxidation state (Katzin 1983). Details of thorium chemistry are given by Katzin (1983).

Table I. Chemical Properties of Various Thorium Salts

Property	Thorium (Th)	Thorium Dioxide (ThO$_2$)	Thorium Nitrate, Tetrahydrate (Th(NO$_3$)$_4$·4H$_2$O)	Thorium Fluoride Tetrahydrate (ThF$_4$·4H$_2$O)	Thorium Carbonate (Th(CO$_3$)$_2$
Molecular weight	232.04[a]	264.04[a]	552.12[a]	380.09[a]	352.06[a]
Color	Gray[a]	White[b]	Colorless[a]	Not known	Not known
Physical state	Solid[a]	Powdery solid[b]	Crystalline solid[a]	Crystalline solid[a]	Not known
Odor	Not known	Not known	Not known	Not known	Not known
Melting point, °C	≈1700[b]	3220 ± 50[a]	500 (decomposes)	100 (-H$_2$O)[a]	Not known
Boiling point, °C	≈4500[b]	4400[b]	Not applicable	140-100[c](-2H$_2$O)[a]	Not known
Autoignition temperature	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Solubility:					
Water	Insoluble[a]	Insoluble[b]	Very soluble[b]	0.017 g/100 cc H$_2$O (25°C)[a]	Insoluble in cold water
Other solvents and organics	Soluble in HCl, H$_2$SO$_4$, slightly soluble in HNO$_3$[a]	Soluble in hot H$_2$SO$_4$; insoluble in dilute acid, alkali[a]	Very soluble in alcohol; slightly soluble in acetone[a]	Insoluble in HF[a]	Soluble in concentrated Na$_2$CO$_3$
Density (g/cm^3)	11.7[a]	9.7[b]	Not known	Not known	Not known
Partition coefficients	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Vapor presure	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Henry's law constant	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Refractive index	Not applicable	2.20 (liquid)[a]	Not applicable	Not applicable	Not applicable
Flash point	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Flammability limits	Not applicable	Not applicable	Not applicable	Not applicable	Not applicable
Conversion factors:	1 pCi = 1.2 fg[c] of Th-228	1 pCi = 1.2 fg[c] of Th-228	1 pCi = 1.2 fg[c] of Th-228	1 pCi = 1.2 fg[c] of Th-228	1 pCi = 1.2 fg[c] of Th-228
	1 pci = 9.1 µg of Th-232	1 pci = 9.1 µg of Th-232	1 pci = 9.1 µg of Th-232	1 pci = 9.1 µg of Th-232	1 pci = 9.1 µg of Th-232
	1 pCi = 48 fg[c] of Th-230	1 pCi = 48 fg[c] of Th-230	1 pCi = 48 fg[c] of Th-230	1 pCi = 48 fg[c] of Th-230	1 pCi = 48 fg[c] of Th-230

[a]Weast 1983
[b]Hawley 1981

[c]1 fg = 10^{-9} µg; 1 pCi = 10^{-12} Ci.

TechXtract® Chemistry Description

The TechXtract® chemical decontamination process is based on hypotheses relating to radionuclide migration and removal. The first is that contaminants migrate along grain boundaries and into pores and microscopic voids (Kirkendall effect) of a solid substrate. Even seemingly non-porous materials, such as stainless steel or plastic, contain these microscopic pathways. Mobility, time, and secondary forces often drive contaminants to deeper underlying levels of the material (i.e. substrate). Furthermore, contaminants tend to become chemically or electrostatically bonded to the substrate through hydrogen bonding. In many cases the exposure time a contaminant has on a substrate allows the migration pathways to

become partially closed again with workplace grime and other non-targeted secondary contaminants. Attacking this problem points to the need for a sequential process that will accomplish all of the following in the correct order.

- Re-open the pores and capillary pathways to the maximum possible extent,

- Penetrate into the pores as deeply as possible,

- Break the electrostatic and chemical bonds which hold the contaminants in place,

- Complex or sequester the contaminants to prevent recontamination, (Affinity Shift)

- Activate the capillary rise effect. (Young and Laplace equation). (Carrier Solution)

TechXtract® does each of these steps, by using 25 different functional groups in each of its three separate chemical solutions. When applied in sequence the chemistries react with each other and with the primary and secondary contaminants on the substrate. Both these reaction products and the original formula components ***dissolve, oxidize, reduce, hydrolyze, decompose, wet, complex, micro-encapsulate and integrate flotation chemistry principles.*** The various formulas use high H^+ and OH^- environments for electron transfer to put a variety of pure elements, oxides, and other compounds into solution. Cations are used for adsorption onto negatively charged substrates. The low surface tension of the blends (typically <10 dyne/cm^2) allows for a low contact angle that creates effective penetration of the capillaries thus allowing for micro-emulsification. Hydrotopes are added to increase the solubility of certain organic compounds. Other components are used to buffer strong acids, so that the blends are non-corrosive.

The "affinity-shifting mechanism" can be theorized by the fact the cleaning compositions perform their function by interaction of basic electro-chemical processes. Contaminated surfaces are usually negatively charged. Therefore, the positive ion-containing cleaning solutions are attracted to the surface by electrostatic effects and attracted into pores and microscopic voids and crevices by both electrochemical effects and electrocapillary forces. Further, the cations in the extraction solutions react electrochemically with the contaminants to solubilize, or leach them out.

The first two chemicals are surface preparation formulas (0300 and 0200), which contain complex blends of acids and other chemical agents to clean dirt, oil, grease and other interferences from the surface. The 0300 serves to oxidize the various isotopic compounds, inorganic impurities, organic impurities, and the physical chemistry of the various substrates to allow for penetration in subsequent chemical treatments. The 0200 reduces various radionuclides and inorganic impurities. It also is partially comprised of etching agents some of which put oxide forms into solution, and promotes radionuclide transport of the target isotope(s) by the addition of sequestering agents.

A blend of the two formulations on a ratio basis prepares the substrate by establishing proper conditions for the extraction step. Each formula has an important role on its own, but when 0200 is mixed in the correct ratio(s) (dependent on the isotope(s) and their oxide forms) with 0300, the resulting complex compounds put even the most insoluble, inorganic oxides into solution. Thus in this step the contaminants have a greater affinity for the solution than the material they were previously bound to.

With the surface now cleaned of all interferences, extraction of the remaining contamination that has migrated into the microscopic pores or voids of the substrate can begin. The 0100 extraction blend provides for the elimination of all interfacial tension and substrate charge to allow the now charge neutral laden solution to flow out of the substrate. The substrate now has a net neutral charge. Amines, a component of the solution provide for desorption of those now mobile radionuclides. Also, in a high pH environment catalysts in the solution promote the formation of free radical hydroxyls which solubilize certain Cs-137 compounds,

Additional components of the formula sequester the contaminants to prevent them from re-contacting and thereby re-contaminating the surface, keeping them in suspension until they can be removed during the rinse step(s). In essence, the extraction solution penetrates below the surface and binds itself to the contaminants, desorbs them, then pulls the contaminants horizontally and vertically through the microscopic pores to the surface using electro-capillary techniques.

The chemical formulations used in the technology satisfy OSHA Section XVIII, 29 CFR 1910.120, containing no hazardous components regarding flammability or reactivity (as per 40 CFR 261). They are designed to prevent the release of any harmful fumes. Even though low and high pH blends are used in the process, pH at disposal is close to 7, and the secondary waste liquids are non-corrosive. This is due to the fact that the chemical blends are designed to react on the substrate(s), e.g. concrete, to become harmless salts. Additionally, these chemical formulas do not contain components that are classified as RCRA hazardous for disposal. As a result, the waste stream from a project can be characterized based solely on the contaminants that were extracted.

The process has been found to be most applicable in remediation or decontamination projects when one or more of the following conditions apply:

- The acceptable level for any residual contaminant is very low (e.g., free release1,000 dpm/100 cm^2 or lower),
- Simple surface cleaning is ineffective,
- Disposal is undesirable, either because the volume and resulting disposal and replacement costs are too high, or due to resource recycle or waste minimization objectives,
- Significant safety concerns - such as flammability, corrosivity, creation of airborne contaminant particles, fugitive emissions or generation of toxic fumes and/or explosive gases - are raised.
- Decontamination is to be performed on surfaces that are not flat and horizontal, such as walls, ceilings, structural beams, and internal piping.

The technology can be used to remove a wide variety of contaminants, especially Co^{60}, Cs^{137}, $Pu^{238-239}$, Am^{241}, and $U^{235-238}$, from porous surfaces and substrates. This is made possible through tailoring of the chemistry and process for individual contaminants and other project-specific factors.

The degree of subsurface penetration is obviously dependent on the nature of the capillary structure. For porous materials such as concrete and wood, very deep extraction is possible. With metals, contaminants become entrapped or bonded in boundary grains and voids, in minor imperfections, and in the oxide layer. EAIGS Client core sampling has shown that the

chemistry is effective in extracting contaminants and cases have been documented where radiological material has been extracted from concrete **at more than two inches below the surface.** In addition to this core data, analyses of the spent chemicals from several projects have shown high levels of the target contaminants, confirming the extraction mechanism. **Results with fixed radionuclides** indicate extensive decontamination, regardless of the depth of the particles.

A unique aspect of the technology is that the extraction occurs in both horizontal and vertical directions further enhancing the effectiveness of the overall process. The process is **not limited to floors or other flat,** horizontal surfaces since the nature of the chemical formulas and application make the extraction technology highly effective on all types of surfaces (**both horizontal and vertical**) and substrates. Successful projects have included decontamination of walls, ceilings, equipment, structural beams, internal piping and highly irregular surfaces, similar to what is required for the chamber decontamination.

Project Description

In the forth quarter of 2003, a manufacturer of Thorium Fluoride coated optics was faced with disposal of its used vacuum deposition chamber. The manufacturing capacity represented by the used installation, was to be replaced with a new unit at a new location. Regulators would not allow the new green field location to install a contaminated unit. The set of circumstances dictated that the manufacturer either decontaminate and move the used chamber, or incur the costs of both the disposal of the existing used unit and the purchase of a new replacement unit. At the time, there had never been a successful decontamination of ThF4 contaminated stainless steel. In addition to the difficulty with the contaminant, any successful procedure would have to leave the vacuum chamber in good working order, capable of meeting the tight tolerances demanded in aeronautic and defense related applications.

Thorium Fluoride decontamination is unusually difficult, and would not normally be attempted if there was not a high value substrate to preserve. The client had attempted various abrasive techniques, but was restricted to less aggressive methods, such as glass beads. These attempts met with marginal success, but were not able to reach the release criteria. A literature search for chemical methods reveals the ThF4 is insoluble in virtually all acids except for hot sulfuric acid. The hot sulfuric acid would not only presented unacceptable safety concerns, it would have complicated disposal by leaving a mixed waste residue, and would have damaged the chamber.

In addition to the Thorium Fluoride, other Thorium salts were present including AuF and MgF. The presence of co-contaminants in workplace decontamination problems is very common and can significantly affect the probability of project success. In this case, the presence of gold salts added another level of complexity to any chemical decontamination scheme. As most of us know, gold is insoluble in all acids, with the exception of a mixture of nitric and sulfuric acids commonly referred to as aqua regia. As noted earlier, these extremely harsh acids were unacceptable as general decontamination agents. However, the co-contaminants still required removal in order to reach the desired decontamination target levels.

Initial scans ranging from 6,000 to 21,000 cpm/100cm^2 were found throughout the inside of the chamber prior decontamination. The chamber was disassembled into individual pieces,

ranging in size from as large as an 8-foot long boom, to as small as individual nuts and bolts. An attempt was made to decontaminate the "partition shield" using glass bead shot. The partition shield is a stainless steel plate approximately four foot square, positioned between the source ThF4 evaporation boats and the chamber door. The initial contaminant level was reduced from approximately 16,000 cpm, but leveled out between 600 and 1,000 cpm, well above the desired background level. It was at this point that a chemical decontamination approach was tried.

The TechXtract® liquid decontamination technology uses sequential chemistry applied as a spray that penetrates into the substrate boundary layer, breaks the electro static bonds holding the contaminant to the substrate, puts the contaminant into solution, and sequesters it preventing re-deposition. The three liquids each have a surface tension under 10 dynes/cm2, allowing penetration even into the boundary layers of stainless steel. This allows for removal of "fixed" as well as smearable contamination. The sequential chemistry application technique creates micro-emulsified reaction products, which further aid in putting the contaminant into solution. The application technique uses three different solutions, 0100, 0200, and 0300. The solutions are applied then removed in sequence. Each solution was sprayed onto the contaminated substrate with a mist sprayer, scrubbed by hand with steel wool, left to "dwell" on the substrate for 5 to 30 minutes, and then it was rinsed off with de-ionized water.

The liquid was applied in a secondary containment structure. Small parts were sprayed in a 2' x 3' x 2' tub. Larger parts were done on polyethylene sheeting with sorbent borders. The liquid volume generated by the process was less than 0.01 US gallons per square foot of area treated, so containment was not a difficult. The small volume of secondary waste generated also kept disposal volume and cost to a minimum.

Table 2 shows the initial demonstration test results for the chemical process. The first four pieces tested met background decontamination levels with a single pass. However, the partition shield proved to be much more difficult. Despite repeated cycles, the 9 different shield areas did not reach background levels. Since these areas were also glass blasted, it is assumed that the blasting sealed the substrate gel pores, preventing the liquid from penetrating. This sheet was the only piece that did not reach background during the test or full-scale project.

Table II. Decontamination Results for TechXtract® Chemical Process

Chamber Part	Initial Scan (cpm)	One Cycle (cpm)	Two Cycles (cpm)	Three Cycles (cpm)	Final Scan (cpm)
Mask Shield (Right)	18,035	3	---	---	<2
Mask Shield (Left)	3650	3	---	---	<2
Side Cover (Top)	21,214	2	---	---	<2
Side Cover (Bottom)	384	2	---	---	<2
Partition Shields					
(a)	903	306	141	60	60
(b)	1104	440	180	106	106
(c)	556	251	141	62	62
(d)	501	206	116	23	23
(e)	632	182	41	21	21
(f)	383	121	71	27	27
(g)	970	462	290	57	57
(h)	427	193	133	29	29
(i)	586	201	119	64	64

The TechXtract®decontamination successfully reduced activity to background, of 2 cpm, without damaging the chamber structures. Total secondary waste volume produced fit into single a 55-gallon drum. The liquid waste was solidified with cement grout for disposal. With the exception of the partition shield, the vacuum chamber was reassembled at its new location ready for use. The full-scale decontamination project was performed by the exclusive licensee of the TechXtract® technology, Environmental Alternatives, Inc. of Keene, NH. Disposal costs were reduced by 75% and remanufacturing costs were entirely eliminated.

CONCLUSION

The TechXtract® chemical decontamination process proved to be a cost effective method for removal of ThF_4 deposition contamination, given the high value of the substrate and the anticipated disposal costs associated with purchasing a new replacement unit. The process also removed co-contaminants, including Fluoride salts of Gold and Magnesium. The process did not damage the chamber's stainless steel while removing the contaminants.