

Evaluation of the Immobilization of Technetium by Incorporation into an Electroless Plated Ternary Alloy - 14179

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ABSTRACT

Technetium (Tc) is a man-made element generated from the fission of ^{235}U -enriched nuclear fuel. The most abundant Tc isotope in nuclear waste is ^{99}Tc , with a high fission yield (~6% of total fission products) and a long half-life (2.13×10^5 years). Tc exists in underground storage tanks at DOE sites, including contaminated nuclear fuel processing facilities and nearby aquifers, and used nuclear fuel. Regulatory requirements mandate its retrieval, processing, and permanent disposal. Tc forms the extremely soluble and environmentally mobile pertechnetate anion and is one of the leading performance assessment concerns at waste disposal facilities. To address the Tc disposal problem, AREVA has developed an aqueous process that eliminates Tc from an aqueous solution and immobilizes it into a metallic waste form. The product may be further immobilized by incorporation into another matrix, such as grout.

Pertechnetate specific ion exchange resins are utilized to sorb Tc from aqueous streams, such as Hanford tank waste, contaminated groundwater, or from used nuclear fuel reprocessing. Tc is eluted from the resin, and plating chemicals are added to the eluate to form the plating “bath”, including a reducing agent, an alloying element, and a complexing ligand at appropriate pH and temperature to spontaneously deposit a ternary alloy. Electroless plating is an aqueous autocatalytic chemical reduction process successfully used to reduce ^{99}Tc (VII) to a metallic Tc bearing alloy film adhering to a prepared substrate. As part of the electroless plating process, the reaction mechanism may proceed by virtue of an in-situ reduction process wherein the alloying transition metal ion is catalytically reduced to its metallic state at the substrate surface and is oxidized in turn by pertechnetate, yielding transition metal ion once again, and reduced Tc. The reaction is allowed to proceed until virtually all of the Tc is consumed and thus incorporated into the plated deposit. Ion beam milling followed by Energy Dispersive X-Ray Spectroscopy (EDS) of a deposit cross section indicates that Tc comprises ~30% of the deposit and oxygen <1%. The absence of any substantial quantity of oxygen indicates that Tc likely has been reduced to its metallic, zero valent form.

After Tc plating is completed, the surface of the substrate is found to be devoid of any smearable activity. Subsequently, the catalytically active substrate is plated in a traditional electroless nickel (Ni) bath to “armor” the Tc layer with a nickel-phosphorus (Ni-P) binary alloy that aids in corrosion resistance.

Samples of the Tc laden substrate have been incorporated into grout (Hanford’s Cast Stone formulation) and allowed to cure for 28 days. The grouted samples contained Tc at the Nuclear Regulatory Commission (NRC) class A limit (0.3 Ci/m^3). Upon curing, the samples were subjected to the American National Standards Institute (ANSI) 16.1 leach procedure. Through the 90 days of leach testing, no leachate sample exceeded the detection level of the available instrumentation ($0.05 \mu\text{g/L}$, or $9 \times 10^{-10} \text{ Ci/L}$).

INTRODUCTION - TECHNETIUM IN RADIOACTIVE WASTE

Technetium (Tc) is a man-made element generated from the fission of ^{235}U -enriched nuclear fuel. The most abundant Tc isotope in nuclear waste is ^{99}Tc , with a high fission yield (~6% of total fission products) and a long half-life (2.13×10^5 years). Tc exists in underground storage tanks at U.S. department of Energy (DOE) sites, including contaminated nuclear fuel processing facilities and nearby aquifers, and used nuclear fuel. Regulatory requirements mandate its retrieval, processing, and permanent disposal. Tc forms the extremely soluble and

environmentally mobile pertechnetate anion and is one of the leading performance assessment concerns at waste disposal facilities. Tc has an inherent high level of reactivity in the presence of oxygen and forms the extremely soluble and mobile pertechnetate anion. Consequently, it is difficult to sequester into a final waste form for geologic disposal. Oxidized Tc compounds are also volatile in thermal processes such as vitrification, resulting in high levels of ⁹⁹Tc in secondary waste streams.

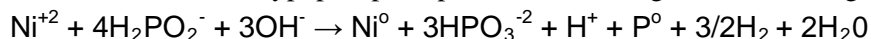
Among the numerous valence states of Tc, two are predominant at standard conditions: Tc(IV) and Tc(VII), with Tc(IV) compounds (such as TcO₂) being far less soluble than Tc(VII) compounds such as NaTcO₄. Proposed waste forms that incorporate ⁹⁹Tc into their structure attempt to take advantage of this fact, by utilizing reducing compounds or elements to form the less soluble Tc(IV), and prevent re-oxidation to the more soluble species. Tc(IV) compounds, in the presence of oxygen, however, can reoxidize to pertechnetate [5]. Previously studied Tc getters include goethite, tin apatite, and zero valent iron. Waste forms and processes investigated for ⁹⁹Tc incorporation include Fluidized Bed Steam Reforming (FBSR), cast stone, ceramacrete, geopolymer, ion exchange resins, and others.

For removal of low levels of ⁹⁹Tc from aqueous waste streams, commercially available anion exchange resins that have a high selectivity for TcO₄⁻ ion have been in use in the DOE complex for a number of years. Several installations of groundwater treatment are in place utilizing non-elutable Purolite A530E anion exchange resin, which was developed at Oak Ridge National Laboratory (ORNL). Elutable Superlig-639 (IBC Advanced Technologies) pertechnetate specific resin has also been tested for use at Hanford's Waste Treatment Plant.

ELECTROLESS PLATING

Electroless plating is the aqueous process of depositing a metallic coating onto a solid substrate without the application of external electrical power, as is used in electrolytic plating. The redox mechanism involves electron transfer between a dissolved metal salt and other reactive chemical species in the plating "bath". Two methods are employed in industrial processes:

- Self-limiting metal displacement *immersion plating* is a process where an aqueous solution of an element that is nobler than that of the plating substrate spontaneously displaces surface metal, forming a thin film of the more noble metal. For example, Immersion Gold processes are used to form a corrosion resistant gold layer on Ni in the electronics industry,
- Self-sustaining *autocatalytic electroless plating* is a process in which electrons are obtained from a reducing agent in solution, rather than an external power supply. In this process, several electrochemical partial reactions occur, including cathodic reduction of metal ions to form solid metal and anodic oxidation of the reducing agent. Thus, when carried out properly, electroless deposition is a process which occurs only on a suitably prepared catalytically active surface and does not occur in the bulk solution. Typical electroless plating processes consist of a solution of transition metal ions (e.g. Ni or cobalt), a reducing agent (e.g. hypophosphite or borohydride), and various stabilizers and complexing agents. Thicknesses of plated deposits range from 10-75 μm and consist of an alloy of the deposited metal and a small amount of an elemental metalloid component of the reducing agent (P in the case of hypophosphite; boron in the case of borohydride). Plating parameters dictate the quantity of these elements, which in turn determines the metallurgical properties. As an example, the reaction with Ni and hypophosphite proceeds according to the following equation:



In this example, the end products of the reaction are a Ni-P binary alloy deposited onto the surface of the substrate, orthophosphite as an oxidation by-product, and a small amount of hydrogen gas. As they are consumed, Ni, hypophosphite, and hydroxide are added to the bath to maintain the autocatalytic reaction.

Electroless plating has distinct advantages over electrolytic plating, namely its simplicity, lack of need for complicated equipment, and the ability to form a smooth and even metallic layer regardless of substrate geometry that is extremely wear and corrosion resistant. Electroless plating has the unique ability to form a metallic deposit on non-conductive surfaces such as glass and plastic, if proper pretreatment methods are employed.

ELECTROLESS ALLOY PLATING

A number of transition metals can be added to the electroless bath for the purpose of creating a multi-element alloy with targeted metallurgical properties. For example, a Ni-W-P ternary alloy can be formed for added heat resistance and Ni-Fe-P is used for its magnetic properties in electronics. Certain transition metals can be alloyed with another metal (such as Ni or cobalt) that would otherwise not plate by electroless means [3-4]. An example of a metal in this group is rhenium (Re). The reaction mechanism may proceed by virtue of an in-situ reduction process [1-2] wherein the alloying transition metal ion is catalytically reduced to its metallic state at the substrate surface and then is oxidized in turn by perrhenate, yielding transition metal ion once again and reduced Re. The end product is the ternary alloy Ni-Re-P.

ELECTROLESS TECHNETIUM PLATING

This paper documents the effort led by AREVA Federal Services LLC (AFS) in Richland, WA, and conducted at the Center for Laboratory Sciences (CLS, Pasco, WA) to immobilize Tc into a metallic alloy utilizing the method of electroless plating, forming a ternary alloy containing Ni, P, and Tc. Preliminary work was conducted using Re as a surrogate for Tc.

Goals of this testing were to:

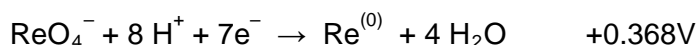
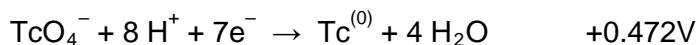
- Use a commercially available low cost substrate as a plating base,
- Establish effective substrate pretreatment steps to properly prepare the surface for electroless plating,
- Electroless plating in a plating bath to preferentially incorporate Re/Tc into a metallic deposit,
- Overcoat the Re/Tc containing metallic film with a high P (>10% P) to provide a highly corrosion resistant surface.

U.S. Patent Application No. 13/964,247, Immobilization of Tc by Electroless Plating, submitted by AREVA Federal Services LLC in August 2013, details the concept of immobilizing Tc into a corrosion resistant ternary alloy.

EXPERIMENTAL

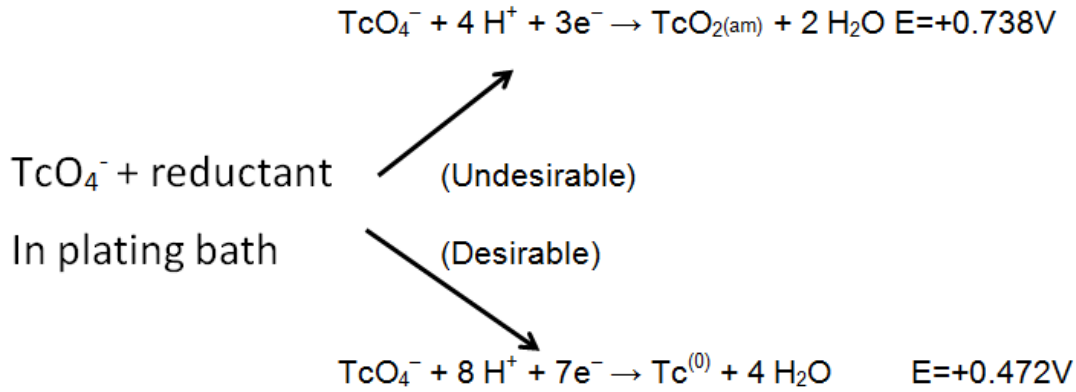
During the research phase of the project and prior to laboratory work, it was determined that the deposition of Tc by electroless means would likely proceed much the same as Re in a preferential manner to that of Ni. The standard potential of Tc, being higher than Re, indicates that Tc should deposit even faster than Re:

Electrochemical Potential, E°



Non-radioactive tests with rhenium successfully showed that Re was deposited by electroless means at a rate up to four times faster than the molar ratio of Ni:Re would indicate, likely due to the higher potential of rhenium. The results of this testing were used to formulate a plating bath for technetium plating, as the technetium, with a potential that is higher still, was expected to plate by electroless means at an even higher rate. This did occur, but

only briefly, followed by complete cessation of Tc reduction within a few minutes of initiation. An investigation of this effect determined that two parallel reactions may be taking place:



Thus, the reaction may proceed in two separate pathways: a desirable reduction from pertechnetate to Tc metal and an undesirable reduction to TcO₂, that may exist as an insoluble colloid [6]. Plating bath conditions were modified to ensure that the Eh-pH conditions were conducive to maintaining Tc in the pertechnetate form for the plating process to proceed to completion.

A prototypical concentration of Tc at 500 mg/l as feedstock in a separate supply container was used as feedstock to the plating bath, which was maintained at ~10 mg/l. Once suitably prepared substrate is introduced, Tc, Ni, and P are electrolessly plated onto the substrate. In this test, the Tc laden solution was fed into the plating bath for a two-hour duration. At this point, the Tc feed was stopped and the electroless plating continued until Tc was reduced to a concentration below the Minimum Detectable Activity of the analytical instrument, meeting the EPA Drinking Water Standard. Results are plotted in Figure 1. This method of slow Tc feed into the plating vessel is necessary due the poisoning effect of the Tc on the electroless plating process. In this test, the poisoning effect took place at approximately 20 mg/l, but is believed to be a function of the ratio of catalytic surface area to mass of Tc. By utilizing this method, much higher concentrations of Tc can be treated without cessation of the plating process.

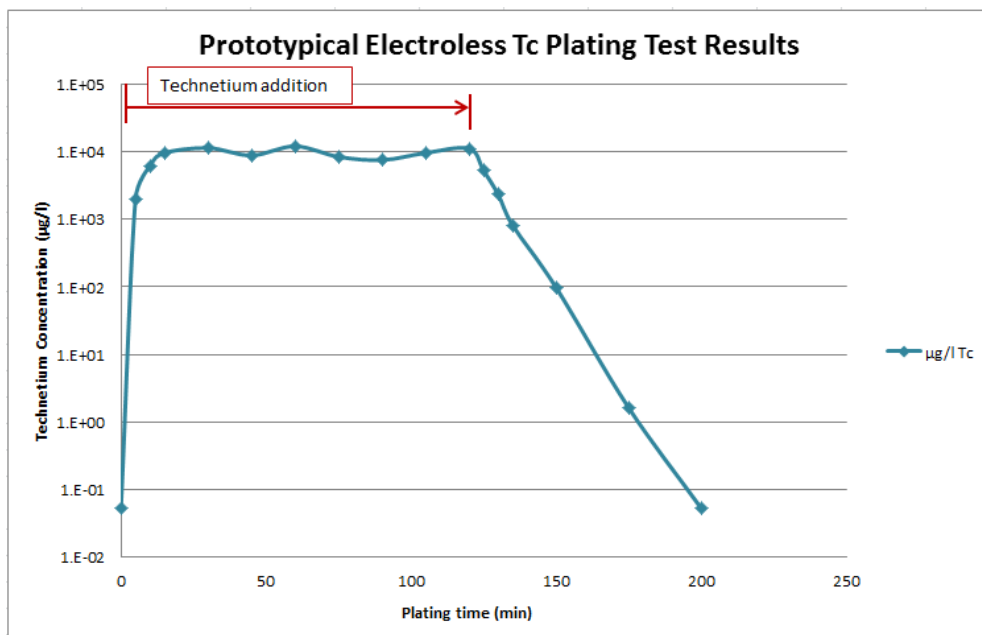


Figure 1: Prototypical electroless ⁹⁹Tc plating results

TECHNETIUM DEPOSIT: MICROSCOPY AND ANALYSIS

Samples were removed from the bath between the Tc plating and the armoring layer, and were imaged with SEM, and the compositional analysis determined by EDS (Figure 2). The roughness of the surface is due to both the polishing process of the stainless steel ball bearings as received from the Vendor and the acid etch pretreatment. The notable lack of a significant amount of oxygen in the EDS spectrum indicates that ⁹⁹Tc has been deposited in its metallic, zero valent form, rather than being adsorbed in an oxidized form onto the surface. Iron and chromium are artifacts from the stainless steel substrate, rather than on the surface of the deposit. The results from the EDS with features <1μm in size will likely also include a component of the surrounding matrix due to electron scatter. Imaging and analysis was performed on a Zeiss SIGMA FE SEM, with an Oxford Instruments EDS and X-Max 20mm SDD, running AZtecEnergy acquisition and analysis software. Calibrations are traceable to NIST standards.

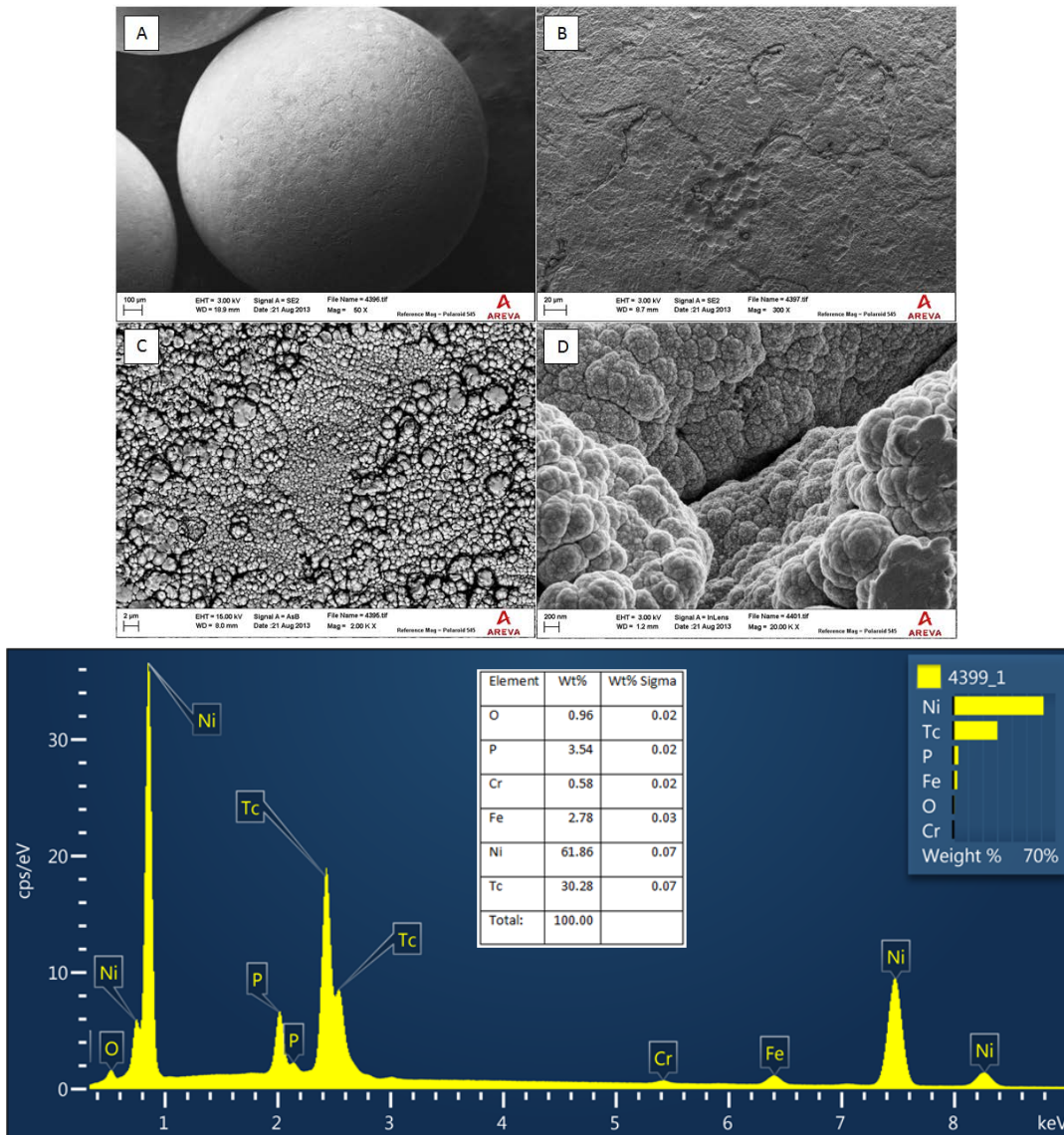
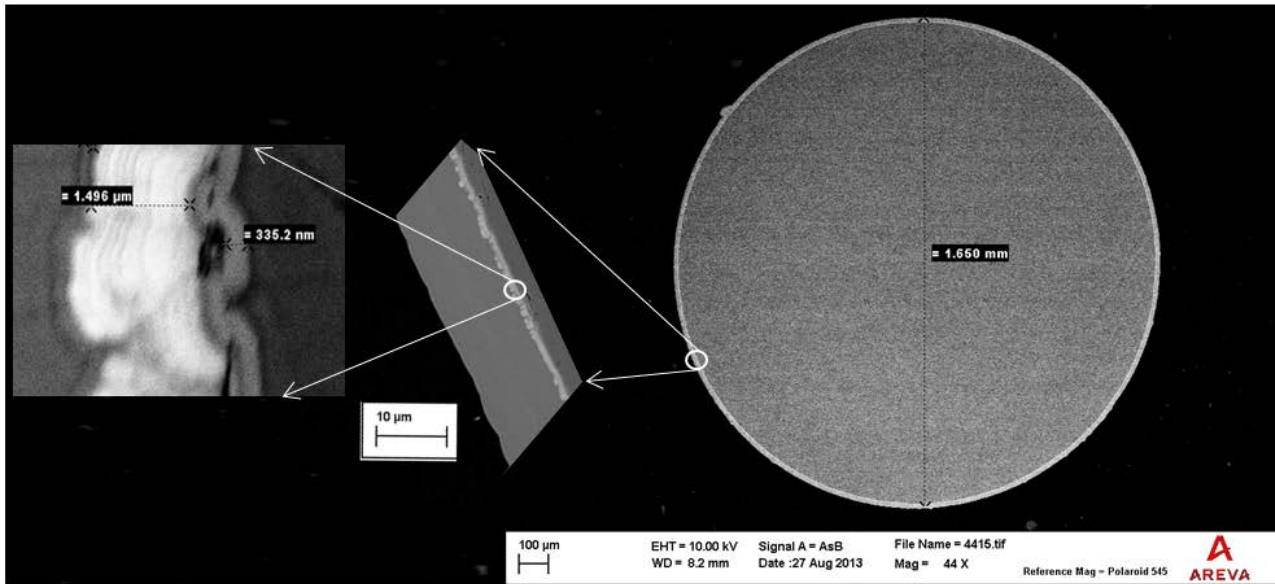


Figure 2: SEM images of the as-plated Ni-Tc-P (A) 50X (B) 300X (C) 2,000X (D) 20,000X, and EDS spectrum of the technetium rich surface.

Samples of the plated substrate with the armoring layer were embedded into a thermosetting epoxy resin with a hot isostatic press, then ground and polished. The cross section and exploded views of the plated layer shows the nickel pretreatment layer at $\sim 0.33 \mu\text{m}$, the ^{99}Tc rich layer $\sim 1.5 \mu\text{m}$, and the armoring layer at $\sim 10 \mu\text{m}$ are shown in Figure 3. Heavy elements (higher atomic number) will backscatter electrons more strongly than light elements (low atomic number), and as such, they appear brighter in the image. In this case, ^{99}Tc has a higher atomic number than the other elements, and thus, appears much lighter.



In Figure 4, the progression of plating from 316L stainless steel substrate to the electrolytic nickel that is needed to catalytically activate the stainless steel, the ^{99}Tc rich layer, and the Ni-P armoring layer can be seen in the line scan. Plating the ^{99}Tc , although effective, is very slow at only $\sim 0.75 \mu\text{m}$ per hour. In contrast, the pretreatment layer is plated at $\sim 30 \mu\text{m}$ per hour, and the armoring layer plates at about $6 \mu\text{m}$ per hour. In all analyses performed, oxygen is present at $<1 \text{wt}\%$ of the deposit, indicating that technetium has been reduced to a metal, and is contained within the Ni-Tc-P alloy. Other images and spectra for the final armoring deposit indicate that there is an absence of ^{99}Tc on the surface of the substrate.

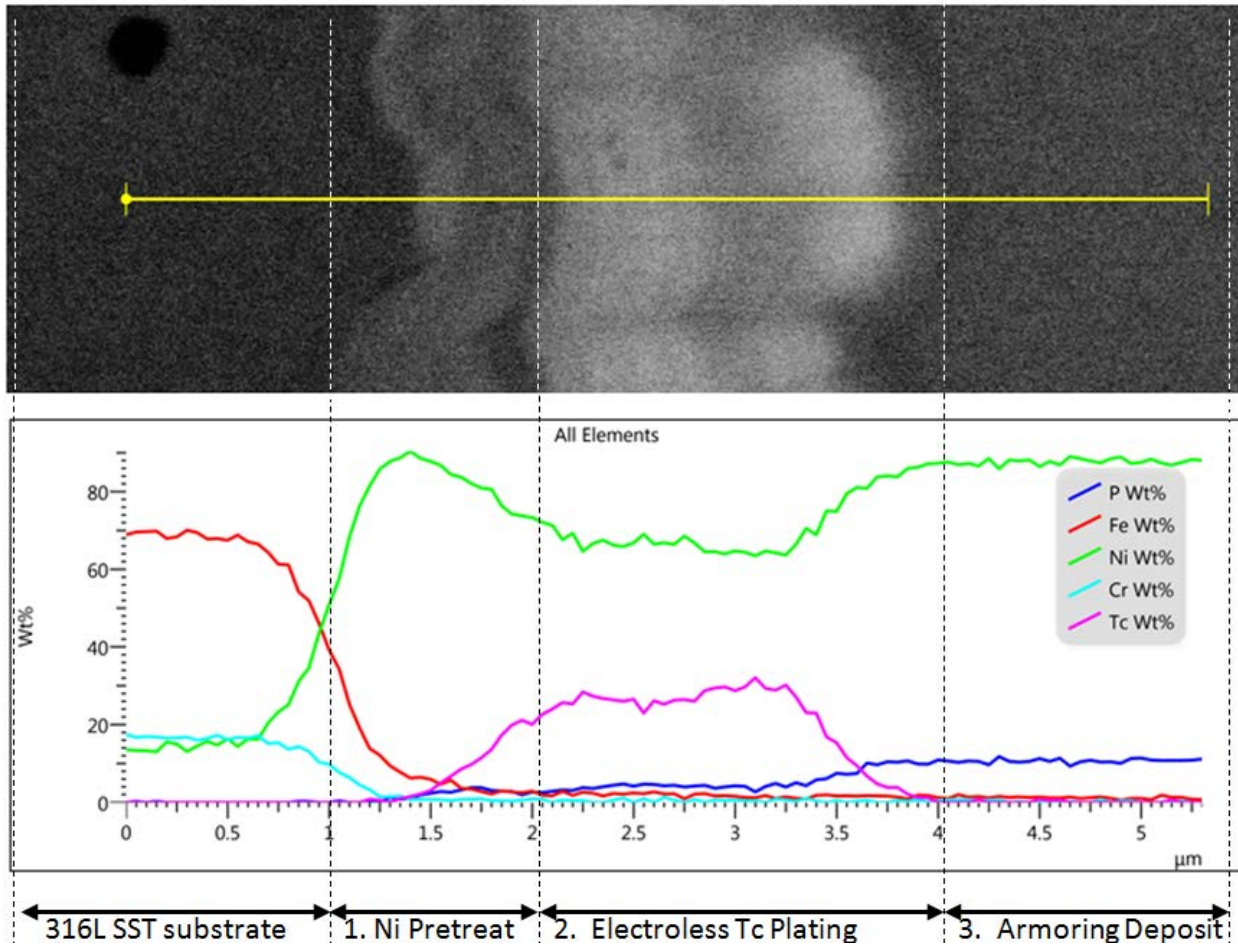


Figure 2: SEM image and EDS line scan of the multi component deposit

CONCLUSIONS AND SUMMARY STATEMENTS

Electroless Tc plating has been successfully demonstrated as an effective means of removing the environmentally troublesome ^{99}Tc from an aqueous solution and depositing it as a metallic ternary alloy with Ni and P. Plating takes place on a catalytically activated substrate and proceeds until Tc is removed from the bath to levels that are typically below the detection limit of the available instrumentation, corresponding to the established EPA Drinking Water Standard of $9 \times 10^{-10}\text{Ci/L}$.

Using rhenium as a non-radioactive surrogate for technetium, a Ni-Re-P alloy was successfully plated on a variety of substrates. Re as a surrogate in electroless plating however, proved to be marginally useful. Under the same conditions as the Re plating process, Tc was likely reduced to both the undesirable technetium dioxide in parallel with the desirable zero valent technetium by way of the autocatalytic electroless plating reaction. Under these conditions, results indicate that approximately half of the Tc is not removed from the electroless plating bath and remains in solution, perhaps as colloidal technetium dioxide. Speciation tests using pertechnetate specific ion exchange resin verified that the portion of the Tc in solution was not in the pertechnetate form. Based on this information, it appears that Tc in the pertechnetate form is desired for the electroless plating process to proceed to completion. Conditions were selected to maintain the plating bath in the proper composition and parameters. These conditions are conducive to maintaining both $\text{Tc}^{(\text{VII})}\text{O}_4^-$ as the primary (and likely only) aqueous species, and, simultaneously maintain a negative redox potential that would allow electroless technetium plating to proceed.

After Tc plating is completed, the surface of the substrate is found to be devoid of any smearable activity. SEM/EDS results reveal that the deposit contains ~30% Tc and <1% oxygen, indicating that Tc has been reduced to its metallic, zero valent form and, along with Ni and P, forms a corrosion resistant ternary alloy. Subsequent to the technetium plating, the catalytically active substrate can be plated in a traditional electroless Ni bath to “armor” the Tc layer with a Ni-P binary alloy that aids in corrosion resistance.

Samples of the Tc laden substrate have been incorporated into grout (Hanford’s Cast Stone formulation) and allowed to cure for 28 days. The grouted samples contained Tc at the NRC class A limit (0.3 Ci/m^3) and have been subjected to leach testing using the ANSI 16.1 method, *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Test Procedure*. Through the 90 day test, no leachate sample exceeded the detection level of the available instrumentation ($0.05 \text{ }\mu\text{g/L}$, or $9 \times 10^{-10} \text{ Ci/L}$).

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