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ELECTROLYTIC DECONTAMINATION OF CONDUCTIVE MATERIALS FOR HAZARDOUS WASTE MANAGEMENT

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Abstract

Electrolytic removal of plutonium and americium from stainless steel and uranium surfaces has been demonstrated. Preliminary experiments were performed on the electrochemically based decontamination of type 304L stainless steel in sodium nitrate solutions to better understand the metal removal effects of varying current density, pH, and nitrate concentration parameters. Material removal rates and changes in surface morphology under these varying conditions are reported. Experimental results indicate that an electropolishing step before contamination removes surface roughness, thereby simplifying later electrolytic decontamination. Sodium nitrate based electrolytic decontamination produced the most uniform stripping of material at low to intermediate pH and at sodium nitrate concentrations of 200 g L^{-1} and higher. Stirring was also observed to increase the uniformity of the stripping process.

Introduction

Electrochemistry represents a viable alternative to existing technologies for decontaminating a variety of radioactive and toxic wastes throughout the nuclear complex. Electrochemical methods produce significantly less waste and can also increase the efficiency of many existing processing technologies.

There are a variety of reasons for decontaminating surfaces, including lowering the radioactive waste categories of items, decontaminating items during processing to remove them from plutonium (Pu) gloveboxes, and enabling the disposition of special nuclear materials. In the past, many material surfaces were cleaned with concentrated acids that in turn produced large amounts of radioactive toxic waste. These acid wash methods are also inefficient for reducing contamination to desired levels.

Electrolytic methods have been shown to be an effective alternative to acid decontamination methods. At the Los Alamos National Laboratory Plutonium Facility, we have been using electrolytic methods to clean a variety of surfaces, including stainless steel and uranium. In addition, some applications of electrolytic decontamination methods have been shown to virtually eliminate primary waste streams. Demonstrations on a neutral pH dissolution of titanium, for example, eliminated the processing

requirement for hydrofluoric acid, which produces a radioactive toxic waste in the existing process.

Electrolytic decontamination is similar to the common industrial practice of electropolishing and is accomplished by applying a low dc voltage through an electrolyte to induce a chemical reaction. Contamination is removed at the anode the working electrode and goes into solution. The cathode, or counter electrode, can be constructed from a variety of materials, but stainless steel is typically used. At the time of this report, sodium nitrate is the electrolyte of choice because the radioactive contaminants form a precipitate. This precipitate formation leads to easy separation of the waste from the solution; thus, the electrolyte solution can be recycled, greatly reducing waste as compared to past acid processes.

To demonstrate electrolytic surface decontamination, we successfully decontaminated oralloy (highly enriched uranium, a special nuclear material) to swipable Pu and americium (Am) levels of ≤ 20 disintegrations per minute (dpm)/100 cm . This level of decontamination is required for shipment of holdings to Oak Ridge Y-12, the nation's disposition site for oralloy. This work started as a joint project with Rocky Flats Environmental Technology Site (RFETS) with a goal of finding a better method of oralloy decontamination than the hot concentrated nitric acid spray leach process previously used at RFETS. We found that not only is the electrolytic method more effective, but that it also forms a solid product that essentially eliminates a primary waste stream.

Industrial Electropolishing

Typical cold rolled type 304L stainless steel has a microscopically rough surface as shown in Figure 1. Allen and Randall[1] have documented many steel surfaces produced by various finishing techniques and have shown these surfaces to be disadvantageous when the material is introduced to a situation where surface contamination with radioactive species may occur. The disadvantage lies in decontamination difficulties related to the entrainment of contamination within these surface cracks and crevices. This is the case when dealing with containers that are designed for long-term storage of special nuclear materials. It is preferable to remove this surface roughness before a possible contamination situation. Furthermore, mechanically polished materials are inadequate because of the many scratches and grooves introduced by abrasives used in the polishing procedure. An electropolished surface, however, is microscopically smooth and creates no surface scratches that could entrap radioactive materials.

In industrial electropolishing methods, the material to be polished is submersed in an electrolyte and anodically polarized. With the passage of current, the surface layers of the metal oxidize to ionic species and then diffuse into solution. Under the appropriate conditions of electrolyte, temperature, and applied current density, high points on the surface are preferentially removed, resulting in a leveling of the surface. Typical conditions for electropolishing are well documented, based on the material to be polished.[2] For stainless steel, the best electrolytes consist primarily of phosphoric and sulfuric acid. For a pretreatment of uncontaminated metal parts, these electrolytes are

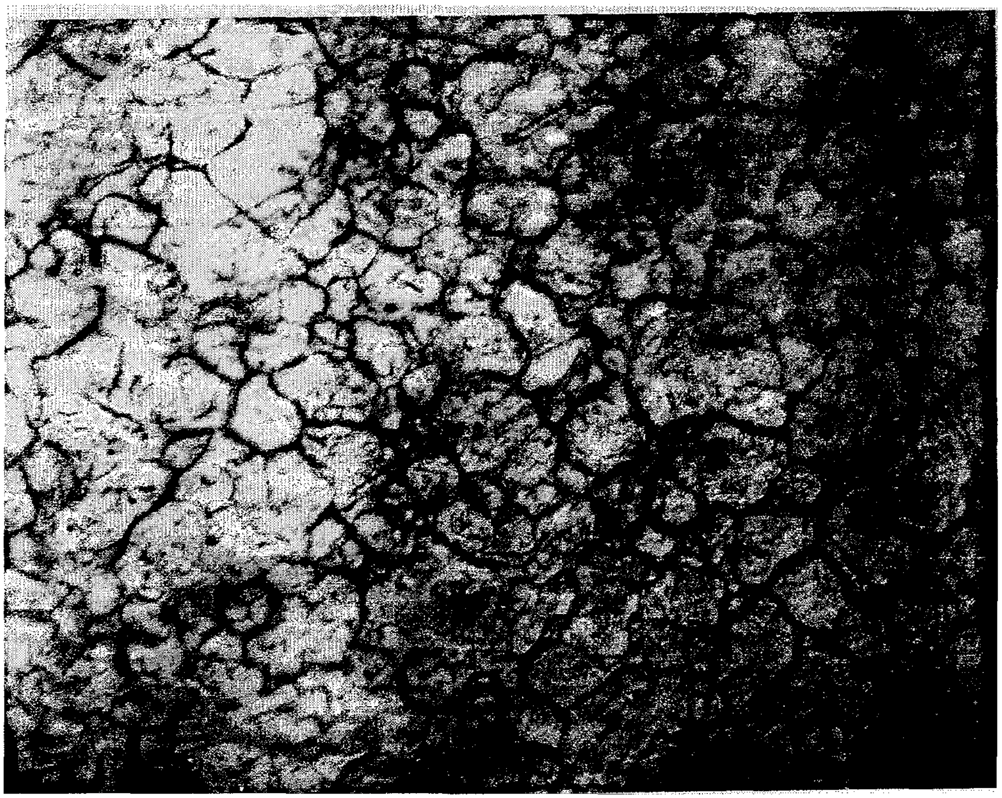

Figure 1. Type 304L stainless steel before polishing (5OOx magnification).

satisfactory. An example of an electropolished 304L stainless steel surface is shown in Figure 2. This sample was prepared by submersing it into a 1:2 mixture of concentrated phosphoric and sulfuric acids and applying a current density of 0.38 A cm^{-2} for a total of charge passage of 300 coulombs.

Once a piece of steel has been contaminated with radioactive species, these industrial electropolishing electrolytes are not desirable. The high acid characteristic of these electrolytes would serve to dissolve oxides of Pu and Am and keep them in solution. After only a few articles are decontaminated, the material buildup within the electrolyte solution would mandate a changing of solutions and result in large quantities of radioactive toxic waste that must be treated and/or disposed. A better solution is to pick an electrolyte with a very low toxicity from which the radioactive materials can be easily separated; thus, the electrolyte can be recycled. Such a choice is a solution of sodium nitrate in water.

Electrolytic Decontamination

Passing an anodic current through a piece of stainless steel submersed in a sodium nitrate electrolyte results in dissolution of the steel. Childs and Winkel[3] have shown that this removal of the surface layers of the steel can result in the removal of surface contamination. At the Los Alamos National Laboratory Plutonium Facility, we have demonstrated electrolytic decontamination of Pu and Am from stainless steel[4] and uranium[5] to contamination levels that enable materials to be removed from glovebox

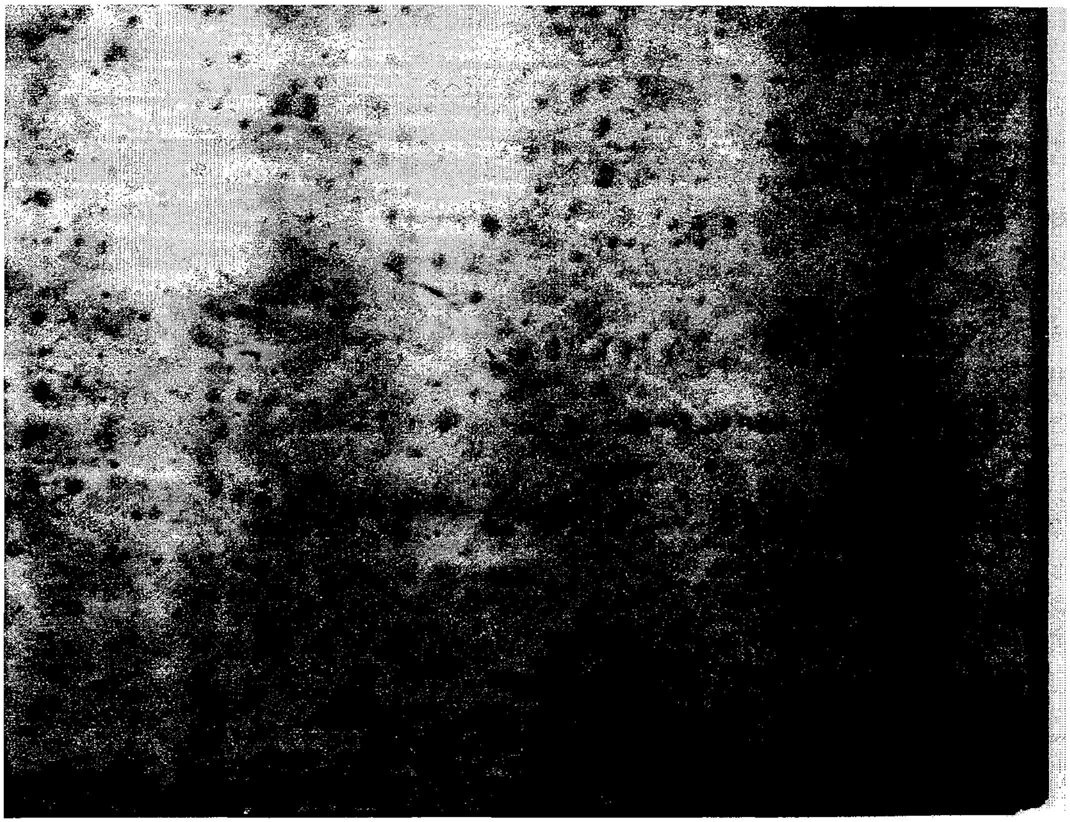

Figure 2. Smooth surface after electropolishing (500x magnification).

containment or that lower the radioactive waste category. For example, we have demonstrated the removal of alpha contaminants, like Pu and Am, from >1,000,000 counts per minutes (cpm) to approximately 1000 cpm by in situ electrolytic decontamination of gloveboxes.[4] (The in situ method allows for the glovebox to remain installed to existing air handling thereby reducing worker exposure and risk during both decontamination and decommissioning.)

Removal of these contaminants lowers the waste category from a transuranic level to low level, greatly reducing disposal costs and enhancing the likelihood of glovebox recycle. Although it is clear that the electrolytic decontamination process works, the chemistry of the process has not been fully characterized. It is the aim of this study to determine the effect of the various decontamination parameters on the rate and uniformity of metal removal.

The dissolution reactions of the steel substrate in the electrolytic decontamination process are identical to those in electropolishing (see Figure 3). However, the difference between the processes is what happens to the components of the steel once they are dissolved. In a solution of sodium nitrate at neutral and higher pH, Fe^{3+} and Ni^{2+} have a very low solubility and hence precipitate as ferric and nickel hydroxides, respectively.

At the current densities of interest and at neutral to high pH, chromium is anodically stripped from stainless steel as hexavalent chromium. In aqueous solution, hexavalent chromium exists primarily as the dichromate ion and therefore will not precipitate with the actinides and other heavy metals; a separation from chromium is therefore possible.

After removal of the other metals by filtration, chromium(VI) can then be converted to chromium(III) by lowering the solution pH and carrying out a reduction.[6] Alternatively, chromium anodically stripped from stainless steel at very low pH and lower current densities is in the 3+ oxidation state.

The other primary anodic process occurring in the cell is the oxidation of water to protons and oxygen gas.

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (1)$$

On the cathode side, the primary reaction is the reduction of water to hydrogen gas and hydroxide ions, though there is also some reduction of nitrate to ammonia. Although hydrogen gas is produced as a byproduct of the electrolytic decontamination process, the rate of hydrogen production is so low that safety is not an issue, even in a glovebox environment.

$$4H_2O + 4e^- \rightarrow 40H^- + 2H_2 \qquad (2)$$

$$NO_3 + 6H_2O + 8e^- \rightarrow NH_3 + 90H^- \qquad (3)$$

Because the primary component in stainless steel is iron, the precipitate is largely composed of ferric hydroxide. This precipitate has a gelatinous nature and tends to incorporate other materials, including actinides, as it precipitates. In this respect, the solution chemistry of the electrolytic decontamination technique is similar to ferric flock procedures that are commonly used on an industrial scale to purify water.

Under conditions of neutral or higher pH there is little chance of dissolution of any contaminating oxides of either Pu or Am on the metal surface. As surface metal is removed, these oxides are freed and can be entrained in the ferric hydroxide precipitate and removed by subsequent filtration. This leaves behind a clean surface, free of contamination. The contaminants are then readily filtered with the precipitating hydroxides, allowing the solution to be reused until the level of dichromate in solution begins to hinder the anodic stripping of the metal. At this point, the solution pH is lowered forcing the dichromate-chromate equilibria toward chromate. Subsequently, the chromate is reduced to chromium(III) through electrolysis or the addition of a reducing agent (e.g., ferrous sulfate) and separated out by precipitation.

The amount of material to be removed from the surface of the contaminated substrate is dependent on the morphology of the surface. If the surface has been prepolished, very little material removal is necessary. For unpolished materials in which the contamination extends to a greater depth due to the roughness of the surface, many more monolayers may need to be removed.

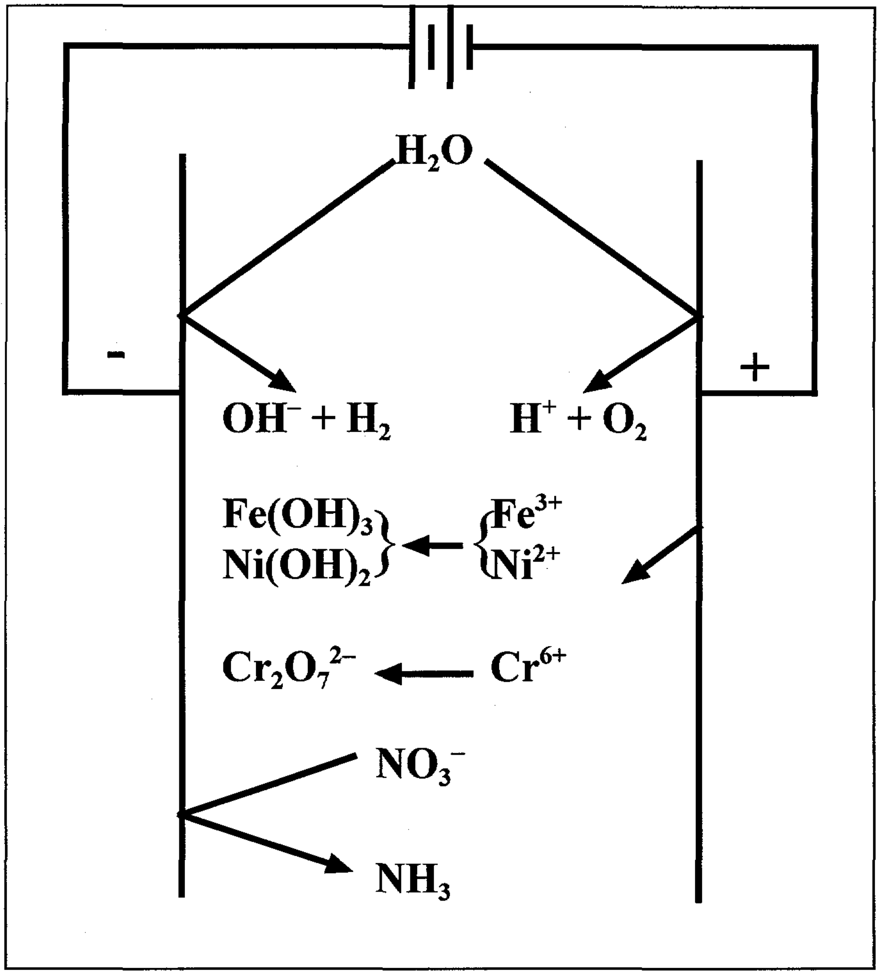

Figure 3. Processes occurring in electrolytic decontamination.

Experimental Procedures

All reagents used in these experiments were general reagent grade or better quality. The electrochemical cell was in all cases a Pyrex beaker. Counter electrodes were stainless steel. All type 304L stainless steel samples were cut from a single sheet of 1/16 inch thickness to a size of 1 cm x 1 cm. All potentials are reported versus a standard Ag/AgCl reference electrode. Applied currents and voltages were supplied via a PAR model 173 potentiostat and a PAR model 175 universal programmer. Current-voltage data was collected on a Houston Instruments Model 2000 x-y recorder. Electrical connections were made to the samples with a copper alligator clip. Precautions were taken to assure that the copper clip remained out of contact with the electrolyte solutions to avoid the stripping of copper metal.

A typical example of the initial surface of the type 304L stainless steel coupons at 500x magnification is shown in Figure 1. This surface is macroscopically rough and visibly dull. As a standard preparation step, all of the samples were electropolished in a 1:2 solution of concentrated phosphoric and sulfuric acids at a current density of

1:2 solution of concentrated phosphoric and sulfuric acids at a current density of approximately 0.38 A cm^{-2} for 300 to 400 coulombs. The resulting surface is microscopically smooth and has a high luster. A typical polished surface is shown in Figure 2.

Several samples were run under various conditions of electrolyte concentration, pH, and current density. The results of these experiments are summarized in Table 1. All samples were examined under a microscope before and after the described experiment. The qualitative result is described under the Results column of Table 1. Surfaces described as smooth are relatively unchanged under examination at a magnification of 500x.

A typical example of a pitted surface is shown in Figure 4. This is the sample resulting from experiment number 17. The best surfaces were obtained at lower pH and at current densities between 0.1 and 0.2 A cm.$^{-2}$ One such surface is shown in Figure 5.

Results

Although there seem to be some spurious data, removal rates were in general found to be highest at higher electrolyte concentrations. Low solution pH also appeared to be favorable for producing high material removal rates. Satisfactory (i.e., > 0.02 $mg \cdot cm^{-2} \cdot C^{-1}$) removal rates occur at sodium nitrate concentration rates of 200 g L^{-1} and

Table I. Summary of experimental data.

Sample	Electrolyte Concentration (g $NaNO_3$ L^{-1})	pH	Current Density (A cm^2)	Metal Removal (mg cm^{-1})	Charge (C)	Resulting Surface Characteristics
1	800	9	0.2	18.4	120	pitted, burned
2	800	9.5	0.5	9.1	90	pitted, burned
3	800	9.5	0.5	9.8	90	pitted, burned
4†	800	< 2	0.5	6.9	60	roughened
5	800	< 2	0.5	7.0	60	roughened
6	800	7	0.2	1.8	60	roughened
7	800	< 2	0.2	6.0	60	smooth
8	100	7	0.2	0.2	60	smooth
9	100	4	0.2	0.3	60	smooth
10	800	7	0.1	2.0	60	smooth
11	800	4	0.1	3.4	60	smooth
12	800	5	0.05	1.8	40	roughened
13	200	4	0.1	0.5	60	burned
14	200	5	0.1	1.21	60	smooth
15	200	9.5	0.2	1.15	60	smooth
16†	600	4	0.2	5.71	60	pitted
17	600	4	0.1	5.15	60	pitted
18	600	9.6	0.1	4.3	60	pitted, roughened

† Denotes no stirring

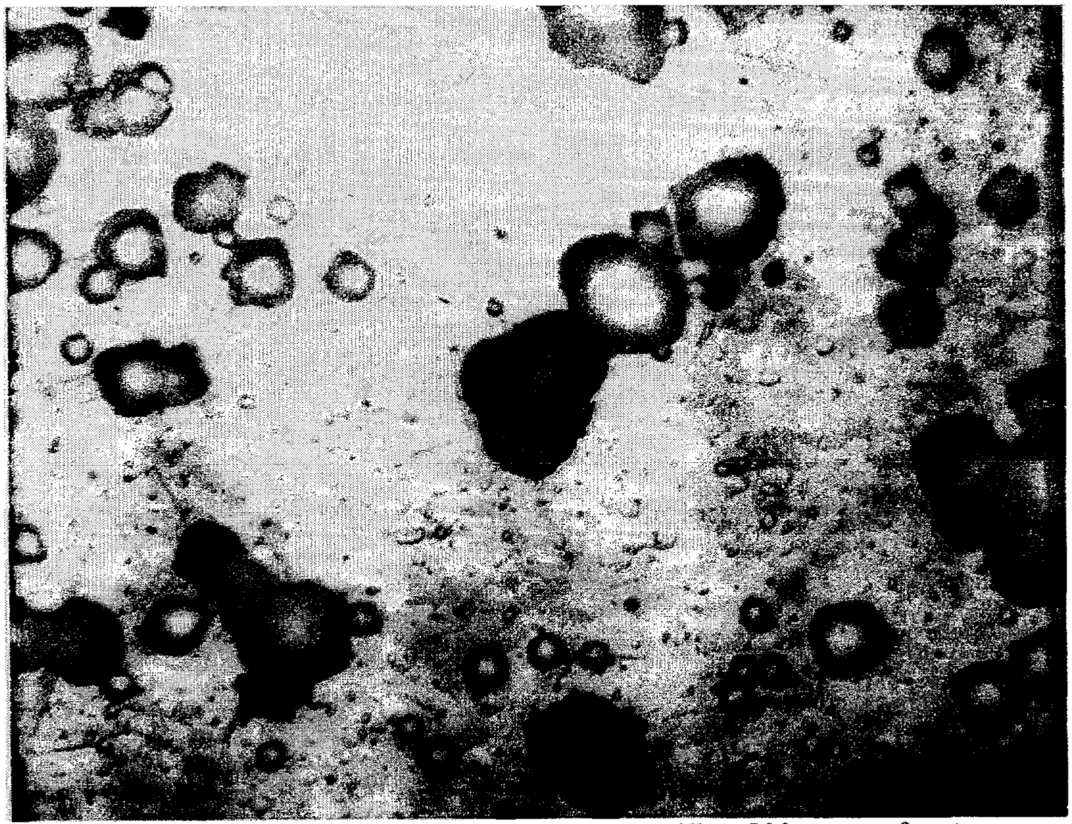

Figure 4. Pitted surface resulting from experiment 17 at 500x magnification.

above. Stirring is also determined to be advantageous in producing a smooth surface. The appropriate current densities appear to be in the range of 0.1 to 0.2 A cm.$^{-2}$ Higher current densities result in higher metal removal rates, but adversely affect the surface morphology by causing roughening, pitting, or burning. These are all indicators of a nonuniform removal. At pH < 2, metal removal rates are high and the resulting surface morphology superb, but precipitation of the removed metal and the actinides does not occur.

Although precipitation of the actinides and transition metals does not occur at low pH, decontamination may still be possible. If the actinides to be removed are present on the surface of the metal as oxides, these oxides may not be dissolved and may enter solution as microparticulates. These particulates may be ultrafiltered and recovered before removal of the dissolved steel components from the solution. The components of steel can then be removed either through electrowinning or by raising the pH of solution to force hydroxide precipitation. From a materials recovery aspect, this is attractive. However, it must be stressed that it is unclear what form the actinides are in once they are freed from the surface. Further studies to examine this issue are required.

We can conclude from this cursory study that the optimum situation for the electrolytic decontamination process is the treatment of metal surfaces that have been electropolished before contamination. Under these conditions, the removal of only a few monolayers of metal should be sufficient for decontamination, because the contamination

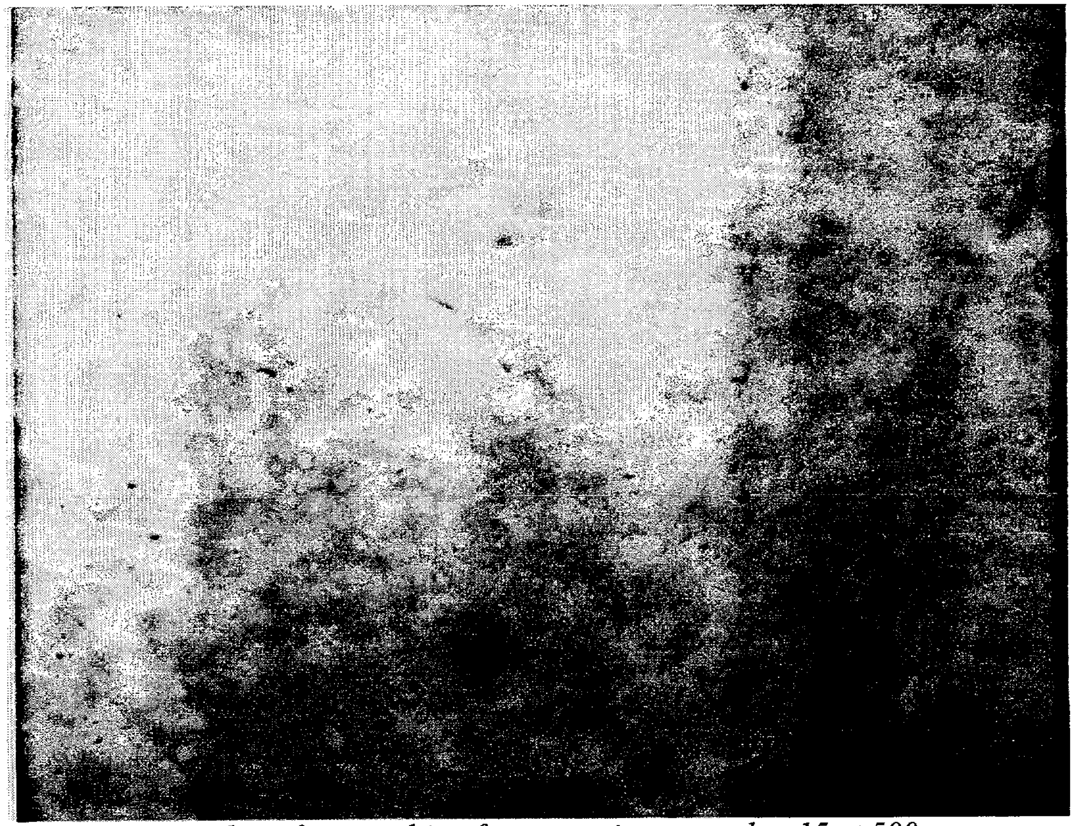

Figure 5. Smooth surface resulting from experiment number 15 at 500x magnification.

is restricted to the microscopically smooth surface of the metal. A five monolayer removal, for example, equates to only about 0.5 g cm^{-2} of type 304L stainless steel.

If a piece of metal to be decontaminated has not been electropolished before its contamination, decontamination is still possible, but requires a greater amount of material removal. The amount of material to be removed under these conditions is reported[3] to be on the order of 2.4 mg cm^{-2}, about four orders of magnitude above that expected for materials receiving an electropolishing before contamination.

Unlike an acid washing process, electrolytic decontamination can be accomplished, no matter how much material removal is required, on a very short time scale and with very little waste generation. Material removal is proportional to the applied current, affording the operator control over the rate and degree of the decontamination.

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