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A COMPARISON OF BULK PRECIPITATED CERIUM OXIDE POWDERS AND CERIUM CONVERSION COATINGS AND THE INFLUENCE OF HYDROGEN PEROXIDE ON THEIR FORMATION (PREPRINT)

S.A. Hayes, P. Yu, T.J. O'Keefe, and J.O. Stoffer

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14. ABSTRACT

To better understand the role of hydrogen peroxide in the formation of cerium conversion coatings and precipitates, hydrated cerium oxide/hydroxide materials obtained from aqueous solutions have been characterized by thermogravimetic methods, X-ray diffraction, and scanning electron microscopy. Powders were prepared by precipitation with sodium hydroxide from cerium (III) chloride solutions using either hydrogen peroxide or oxygen sparging to oxidize Ce(III) species to Ce(IV) species. Cerium conversion coatings were deposited on Al 7075-T6 substrates using a spontaneous immersion process in a water-based solution containing CeCl3 and hydrogen peroxide. The results suggest that the cerium powders produced in the presence of hydrogen peroxide bear the most resemblance to the cerium conversion coatings, and that simulating the cerium conversion coating process through bulk precipitation tests is reasonable. Other significant observations were also made. One was that hydrogen peroxide lowers the pH required to precipitate cerium. Another was that a significant amount of oxygen was evolved upon heating both the cerium conversion coating and the cerium precipitates formed by using hydrogen peroxide as an oxidant. Lastly, the effect of hydrogen peroxide in the cerium conversion coating process is considered from the standpoint of corrosive attack on the aluminum substrates.

15. SUBJECT TERMS

Precipitation, conversion coatings, corrosion protection, cerium

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1. Introduction

Chemical conversion coatings are commonly used on various engineering alloys, particularly high-strength aluminum alloys, to improve paint adhesion and provide corrosion protection. The most widely used conversion coating for aluminum is produced by a chromating processes. Protective chromate layers are usually obtained by immersion of the cleaned alloy in an acid or alkaline solution containing hexavalent chromium, Cr(VI), which provides active corrosion protection. Unfortunately, many Cr(VI) compounds are known carcinogens [1-2]. Also, increased regulatory pressure will make the use of chromium-containing protection systems cost-prohibitive due to increased costs associated with worker protection and waste stream disposal [1]. Many alternatives to chromium corrosion protection systems have been investigated [3-10], but none offers the protection or ease of application of chromate coatings.

One of the more promising replacement systems is based on rare-earth compounds, particularly the cerium compounds. Several researchers [11-14] have demonstrated that treatments with aqueous solutions of cerium salts effectively inhibit the corrosion of aluminum alloys. In the earlier studies, the conversion coatings were obtained by prolonged immersion in hot aqueous solutions of rare earth ions [13, 15-17]. Later, conversion coating processes using solutions of cerium (III) chloride and hydrogen peroxide were developed to produce coatings on aluminum alloys such as 7075-T6 in much shorter time [18-22]. In a cerium conversion coating bath, it is believed that corrosive attack in anodic areas of the substrate is coupled with the cathodic reactions elsewhere on the surface. These cathodic reactions increase the pH at local cathodes, and the increase in pH then leads to the precipitation of cerium oxides/hydroxides [22].

While it is know that hydrogen peroxide can aid in producing a cerium conversion coating much more quickly [22-24], there is a need for a more detailed study of the role of hydrogen peroxide in the process. Besides the aforementioned oxidation of Ce(III) to Ce(IV), other possible effects of hydrogen peroxide on the cerium conversion coating process include changes in the pH at which cerium precipitates [25], complexation or reaction to form cerium peroxide complexes or cerium peroxide species [26-31], and influencing the corrosive attack on aluminum. The thermodynamics of the cerium/water system and of the cerium/water/hydrogen peroxide system have been reviewed elsewhere

[25, 32]. The purpose of this paper is to characterize bulk cerium precipitates formed in the presence of either hydrogen peroxide or oxygen sparging and to compare these results with the characterizations of a cerium conversion coating formed in a peroxide containing solution.

2. Experimental Procedure

2.1 NaOH Titration Curves for CeCl3, With and Without Hydrogen Peroxide

Precipitations were conducted at 25∀1oC using 100mL of 10mM aqueous cerium chloride solutions. CeCl3 was from Alfa Aeser, 99.9 % ultra dry. To prevent premature precipitation—a problem with the peroxide containing solutions—solutions were acidified to a pH of 1.2 using 4 mmol of concentrated HClO4 (Alfa Aeser, 60 % HClO4). For the peroxide containing solutions, H2O2 (Fisher, 31.0 %, ACS) was added in a 10:1 molar ratio of peroxide to cerium. The non-peroxide containing solutions were sparged with 99.95% purity oxygen gas. To increase pH and precipitate cerium, a concentrated NaOH (Alfa Aeser, 10.0 N) solution was added by an Eppendorf repeater pipette in 10 or 20µL increments to the vigorously stirred cerium solutions.

2.2 Preparation of Cerium Oxide Powders and Conversion Coating

To better understand the possible role of hydrogen peroxide in the cerium coating process, three types of powder samples were prepared. One was a powder collected from scrapings of a cerium conversion coating. The two other samples were powders precipitated from CeCl3 solutions with and without hydrogen peroxide present. Materials used were 10.0N NaOH, Alfa Aesar; 30% H2O2 Certified ACS grade, Fisher; and 99.9% CeCl3•XH2O, Alfa Aesar where X was assumed to be 7 for calculating concentration of the final solution. Aluminum substrates were 7075-T6 from Kaiser. Descriptions of the individual samples follow:

2.2.1 Preparation of Cerium Oxide with Oxygen Gas as the Oxidant

Cerium oxide/hydroxide was prepared by rapid addition of a slight excess of NaOH to a CeCl3 solution with oxygen sparging. Sparging was continued for approximately eight hours before the precipitate was filtered and rinsed. Final pH of the solution was between 9 and 10 before rinsing. After drying for three days at room temperature and grinding with a mortar and pestle, the resulting precipitate was light yellow.

2.2.2 Preparation of Cerium Oxide with Hydrogen Peroxide as the Oxidant

Another powder sample was prepared by rapid addition of NaOH to a solution of CeCl3 and H2O2. After addition of base, the sample was stirred for about eight hours before filtering and rinsing. Final pH was between 9 and 10 before rinsing. After drying at room temperature for three days and grinding, the sample was a dark orange.

2.2.3 Preparation of Cerium Conversion Coating

CeCC’s were produced on 7075-T6 substrate by immersing 3”x 6” panels in a cerium chloride solution identical to the solution described previously in section 2.2.2 for the synthesis of the orange precipitated powder. The substrate pretreatment included alkaline cleaning (Turco NC-LT, 5 minute immersion at 55oC) followed by deoxidation with a non-chromated deoxidizer. Immersion time in the conversion coating solution was 30 minutes. The coatings appeared thick, powdery, and orange. After drying in air for several hours, the cerium coating was removed from both sides of the substrate with a utility knife blade, taking care to avoid removal of the underlying aluminum. Eight 3”x6” panels yielded about 0.5g of sample, total. The scrapings were dark orange, similar to the color of the precipitated powder from the hydrogen peroxide containing solution.

2.3 Instrumental Analyses

To determine microscopic morphology and elemental composition, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses were performed in a Hitachi 4700 field emission scanning electron microscope with a Phoenix system by EDAX. Information about the samples’ crystal structure was determined by x-ray diffraction (XRD), using a Scintag XDS200 diffractometer with a Cu radiation source and liquid nitrogen cooled Ge detector. Where possible, crystallite size was estimated via the Scherrer equation using MDI Jade 5.0 software. A Gaussian correction was applied for the instrumental line broadening utilizing NIST standard silicon powder SRM 640B. For weight loss measurements, thermo gravimetric analysis (TGA) was performed under argon using a Netzsch STA 409. The heating rate was 10oC/min. Prior to TGA experiments, samples were stored for at least two days in a desiccator. All samples were analyzed within ten days of production. To identify gases produced when the samples were heated, the TGA instrument was connected to a Netzsch QMS 403C mass spectrometer (MS).

2.4 Simulated Conversion Coating Baths without Cerium

To test for the possible influence of hydrogen peroxide on aluminum oxidation in cerium conversion coating baths, simple aqueous solutions were made to approximate the chloride concentration and pH of cerium chloride based baths, but without cerium. This was done by making two 800mL solutions of 0.39M NaCl. To one of these was added 2mL of 30% hydrogen peroxide (Certified ACS grade, Fisher). At this point, both solutions were acidified with concentrated HCl (Fisher ACS reagent grade) to a pH of 3.2. Immediately prior to immersion of substrates in the simulated, cerium-less conversion coating baths, 3”x6” substrates of aluminum 7075-T6 alloy were solvent cleaned with acetone and cleaned in a commercial alkaline cleaning bath, TURCO 4215 NC-LT. During and after the 30 minute immersion period, substrates were visually examined for signs of corrosion.

3. Results and Discussion

3.1 Precipitation Behavior with and without Hydrogen Peroxide

The pH at which complete precipitation of Ce occurs is lowered when hydrogen peroxide is added to a solution of cerium chloride. In Figure 1, the titration curves for three solutions are shown, plotting equivalents of sodium hydroxide added versus pH for an acidified solution of cerium chloride sparged with oxygen, an acidified solution of cerium chloride with a large (10:1 molar ratio of H_2O_2 to Ce) excess of hydrogen peroxide added, and an acid solution without cerium. Concentrations were chosen such that three mmol units of base (mmol of NaOH on the plot) would completely precipitate Ce(III) from the solution.

The initial cerium species are in the 3+ oxidation state, while the final product is in the 4+ oxidation state. However, the oxidation of Ce(III) species to Ce(IV) species by either oxygen or hydrogen peroxide does not require another equivalent of base for precipitation of a Ce(IV) hydroxide or oxide hydrate. This means that three equivalents of base per unit of cerium are required to completely precipitate cerium from solution, whether the oxidizing agent is O2 or H2O2. For oxidation by oxygen, the expressions are:

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(1) **Error! Objects cannot be created from editing field codes.**

(2)

Assuming that the oxygen partial pressure is 1 and the activity of the Ce(OH)4 precipitate is 1 after precipitation has begun, then:

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(3)

The expressions for oxidation of cerium by hydrogen peroxide would be:

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(4)

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(5)

Assuming the activity of the Ce(OH)4 precipitate is 1 after precipitation has begun, then:

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(6)

From the acid titration curve, it can be seen that all of the added perchloric acid is consumed after four equivalents of base have been added. The same is seen for the acidified, oxygen sparged cerium chloride solution, except that the pH plateaus at 5.2 – 5.8, which is close to the pH of 5 predicted by equation 2. This plateau is due to cerium consuming hydroxide and buffering the solution until Eq. 1 has gone to completion. The third titration curve shows the pH lowering effect of the peroxide addition. Most of the cerium is precipitated in a pH range of 2.0 to 4.0 with hydrogen peroxide present. A more detailed treatment of Ce(III) and Ce(IV) equilibria with hydrogen peroxide in aqueous solution can be found elsewhere [25].

The precipitation curves shown in Figure 1 suggest that hydrogen peroxide can change the conversion coating process since its presence would lower the pH required for the precipitation of cerium compounds onto the substrate. The characterization studies discussed in the following sections indicate that bulk precipitations may indeed be a good way of probing the reactions occurring during the conversion coating process. It will be shown that the cerium conversion coatings formed in the presence of hydrogen peroxide best resemble precipitates formed in the presence of hydrogen peroxide rather than cerium precipitates formed with only oxygen present as the oxidizing agent.

3.2 X-Ray Diffraction Studies of Cerium Conversion Coating and Precipitated Powders

Figure 2 compares X-ray diffraction (XRD) patterns for each of the three powder samples. Scrapings of the cerium conversion coatings were required since the intact films on the substrate were too thin and to produce usable diffraction patterns. The precipitate formed in the presence of oxygen sparging gives much sharper peaks than the sample precipitated from the peroxide containing solution or the sample of cerium conversion coating scrapings. For the oxygen sparged sample, the Scherrer equation was used to estimate an x-ray coherence length of about 2.5 nanometers. The peaks in the patterns for the other two samples are much too broad to make any reliable calculations. But it is obvious that the addition of peroxide has decreased the x-ray coherence length, either by decreasing particle size, or by increasing the number of defects in the structure. The latter possibility is given more credence by the TGA-MS results presented in section 3.4. One other fact should be mentioned. The XRD pattern for the cerium conversion coating shows no peaks for metallic aluminum. This means that very little of the underlying aluminum substrate was removed when harvesting the conversion coating.

3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Morphologically, little difference was seen with SEM between the two precipitated samples and the cerium conversion coating sample. Figures 3a, 3b, and 3c give a comparison of the two precipitated powders with the intact conversion coating. All three samples appear to be made up of agglomerations of much smaller particles. Figure 3d is a micrograph of the cerium conversion coating scrapings. Two points are significant here. One is that the conversion coating seems to be homogeneous through out the bulk of its thickness, and two, there were no metal shavings observed. This is important because multiple EDS samplings measured aluminum concentrations from 2 to 30 weight percent. If this had been from aluminum shavings, they would most likely have been observed in the SEM analysis, or they would have led to very sharp peaks in the XRD patterns discussed in section 3.2. These two facts together point to aluminum present as amorphous aluminum compounds, possibly hydroxides, which could have been produced during the conversion coating process or were derived from hydration of the native aluminum oxide coating.

3.4 Thermo-Gravimetric Analysis Coupled with Mass Spectrometry (TGA-MS)

TGA data for the two precipitated samples and the cerium conversion coating scrapings are presented in Figure 4. The precipitate from the oxygen sparged solution underwent a weight loss of about 11%. The precipitate from the hydrogen peroxide containing solution underwent a weight loss of about 17%. From similar experiments (unpublished data), this has shown to be reproducible to about + 3%. The cerium conversion coating exhibited a weight loss of 34%. A few earlier researchers working with rare earths had hypothesized that cerium could form either complexes (26-31) with hydrogen peroxide or react with hydrogen peroxide to give cerium peroxide compounds. For this reason, mass spectrometry (MS) was used to analyze the gases produced during the TGA experiments.

During TGA analyses, gases from all three samples were continuously analyzed by mass spectroscopy (MS). Initial survey data showed that the major peaks consisted of M/z's consistent with the parent ions and fragments for H2O and O2. The results are presented in Figures 5 and 6. The signal is plotted as ion current, which has also been recalculated to help negate differences in sample size. The results presented should not be interpreted as being highly quantitative, but they do show that the powder precipitated with oxygen sparging lost a very small amount of oxygen as compared to the other two samples, i.e., the powder precipitated in the presence of hydrogen peroxide and the cerium conversion coating scrapings. Also, the relative amount of O2 evolved from the latter two powders is similar, suggest related a similar structure or similar chemical compositions.

The identification of oxygen evolution from the cerium conversion coating sample provides strong evidence for the presence of either a peroxide complex, or perhaps more likely for a dried sample, a cerium peroxide compound. This result could have strong implications in the use of cerium to produce protective coatings. Cerium coatings produced using processes involving hydrogen peroxide would be expected to have much more potential reactivity than processes that result in ceric hydroxide or ceric oxide hydrates. Furthermore, presence of the cerium peroxide species could also explain the differences in the x-ray diffraction data. Peroxides species or their decomposition might lead to defects in the crystal structure of the ceric oxide, and thus decrease the x-ray coherence length of cerium compounds precipitated in the presence of hydrogen peroxide.

In contrast to the data for O2 evolution, the amount of H2O lost varied greatly between the three samples. A greater loss of water appears to explain at least part of the difference between the cerium conversion coating scrapings and the precipitated samples. It would have been expected that given the other experimental results, the water losses would have been the most similar between the cerium conversion coating scrapings and the powder precipitated in the presence of hydrogen peroxide. One reason for this difference may be the presence of impurities in the cerium conversion coating sample. These impurities would likely be amorphous aluminum hydroxides and the water that could have been trapped inside of gel like material (see sections 3.2 and 3.4). Also implying that some of the water is coming for a different source for the conversion coating sample is the difference in the regions for the water loss as shown in Figure 5. For both precipitated samples, water loss commences around 100oC and ends by about 200 to 225oC. The water loss for the conversion coating also commences around 100oC, but it does not begin to taper off significantly until about 350oC. This could possibly explained by the weight loss of aluminum hydroxide in this region [33].

Another important comment should be made. Commonly, the fully hydrolyzed Ce(IV) species precipitated from aqueous solution is usually represented as Ce(OH)4 or CeO2·2H2O, which are equivalent from the standpoint of water loss upon heating. According to the equation

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(7)

the weight loss should be 16%. While the cerium sample precipitated in the presence of hydrogen peroxide comes very close to this, from the TGA-MS results showed that a significant fraction of this weight loss could potentially be the result of oxygen loss and not water. Also, thus far in expanded precipitation studies using other salts, the weight loss for cerium precipitates with sparged oxygen gas as the only oxidant have produced TGA weight losses of only about half of what is predicted by Equation 7., Other interesting experimental observations have included that when cerium is precipitated from chloride solutions with peroxide present, the precipitate is invariably bright orange, whereas if peroxide is not present and Ce(III) species are oxidized only by O2 from air or by sparging, the precipitates are light yellow. The orange precipitates and conversion coatings evolve oxygen as identified by mass spec analyses. Also, the orange powders or conversion coatings will be seen to evolve gas when heated in water at temperatures above 70oC. When the gas evolution has ceased, the orange product will have changed color to a bright yellow. Color does seem to be a qualitative indicator of the potential for oxygen evolution when some samples are heated.

3.5 Possible Effect of Hydrogen Peroxide on the Corrosion of Aluminum in a Cerium Conversion Coating Bath

As described in section 3.1, it is thought that the cerium conversion coating is deposited as a result of precipitation due to an increase in the interfacial pH between the substrate and the bulk solution. The pH increase is due to cathodic reactions, but there must be anodic reactions to produce the electrons consumed by the cathodic reactions. For an aluminum alloy, dissolution of aluminum itself or more active alloying elements such as magnesium would be the likely anodic reactions. Exposed aluminum tends to form passivating oxides that prevent further aluminum oxidation unless the oxide film is prevented from forming or is breached. Fluoride is known to promote dissolution of aluminum, and is used as a surface activator in chromate conversion coating processes Due to the extremely low solubility of CeF3, most cerium conversion coating processes use another halide, chloride, in their formulations. Another possible effect of hydrogen peroxide may be that it promotes the attack of chloride on aluminum.

To see if hydrogen peroxide might indeed act in this way, the following scheme was devised, requiring two solutions with similar composition to cerium conversion coating baths, except without the cerium. This is needed because from the data presented in section 3.2, it is already established that peroxide could increase the coating rate simply by lowering the precipitation pH.

Two solutions of sodium chloride were made to approximate the concentration of chloride found in a chloride-containing, cerium conversion coating bath [14]. To one of these was added hydrogen peroxide in the recommended concentration range. After addition of peroxide to one of the solutions, both were acidified with HCl to a pH of 3.2, which is also within the range of the coating baths. Substrates of aluminum 7075-T6 alloy were solvent cleaned with acetone and cleaned in a commercial alkaline cleaning bath, TURCO 4215 NC-LT. The aluminum substrates were then immersed in the two cerium-less simulated conversion coating baths. The substrates placed in the peroxide containing bath showed signs of corrosive attack almost immediately. Darkening and pitting was clearly evident after a few minutes. Gas evolution was also visible, but since this could have been the result of oxygen evolution by hydrogen peroxide disproportionation as well as corrosive attack, this was not considered to be a conclusive sign of corrosion. The alloy substrates placed in the bath without peroxide showed minimal visible signs of corrosive attack (brightening, darkening, gas evolution, or pitting) after thirty minutes. This result suggests that hydrogen peroxide could promote the corrosive attack of aluminum under conditions present in a cerium conversion coating bath when chloride is present. This in turn could increase the deposition rate of the cerium conversion coating, meaning that hydrogen peroxide could affect the coating process in additional ways to reacting with cerium as mentioned in 3.1.

4. Conclusions

The effects of hydrogen peroxide on the formation of cerium conversion coatings were explored by conducting titration tests and by comparing two types of bulk precipitated powders with a cerium conversion coating. The two types of precipitated powders differed in the choice of sparged oxygen or hydrogen peroxide as oxidizing agents for Ce(III). Results indicated that the presence of peroxide could have the following effects on precipitated cerium compounds: a) it lowers the precipitation pH, b) it decreases the crystallinity of the precipitate as measured by X-ray diffraction patterns, c) it increases the weight loss of the precipitated cerium materials upon heating, and d) forms a phase that evolves oxygen when heated. The oxygen evolution suggests the presence of a peroxide-containing cerium compound. No major differences in morphology were discernible by SEM. Also, with the exception of aluminum content and weight loss, it was observed that the bulk precipitated powders from solutions containing hydrogen peroxide were similar to the cerium conversion coatings whereas the powders formed in O2 sparged solutions were significantly different. The cerium conversion coatings and the precipitated powders from the hydrogen peroxide containing solution had similar morphology, x-ray diffraction patterns, and amounts of oxygen and water evolved during heating. Given the physical similarities of the cerium conversion coatings and the precipitated powders from the hydrogen peroxide containing solution, it appears that bulk precipitations is a valid way to model the cerium conversion coating process.

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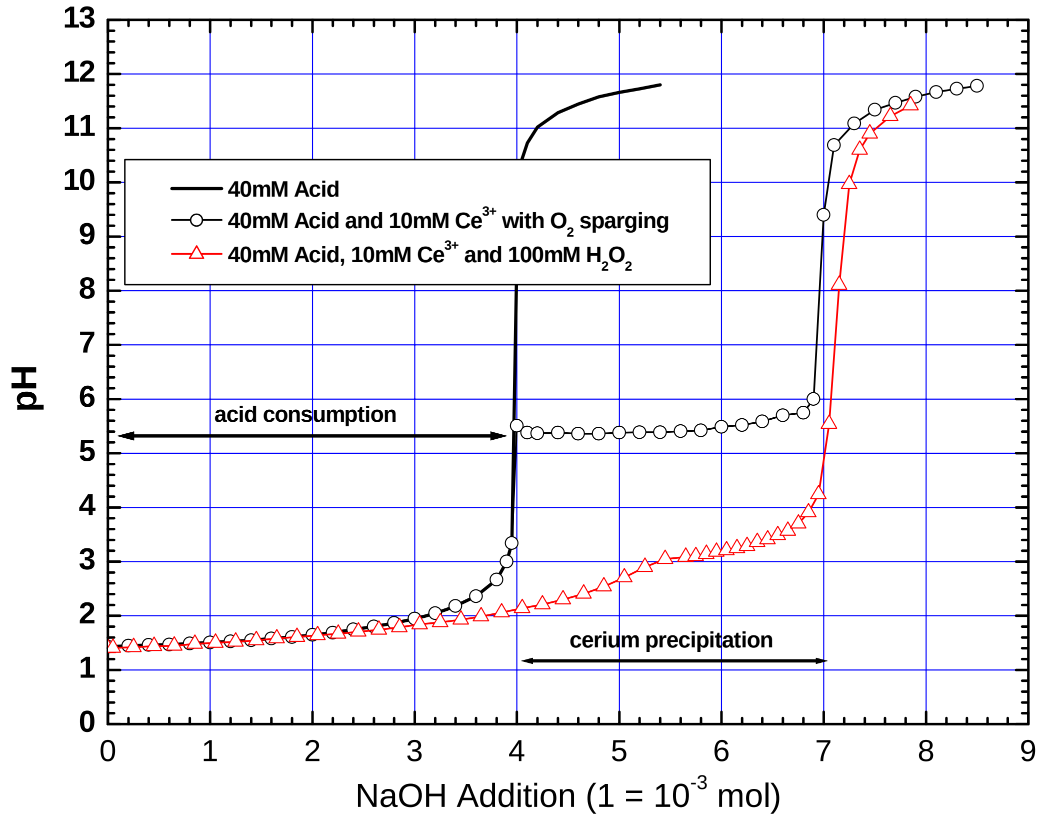

Figure 1. Titration Curves for Cerium in the Presence of Either Hydrogen Peroxide or O_2

Titration curves of 100mL of acidified cerium chloride solutions showing how hydrogen peroxide lowers the precipitation pH for cerium. Solutions were 100mL, stirred, at approximately 25°C. Cerium was added as $CeCl_3$.

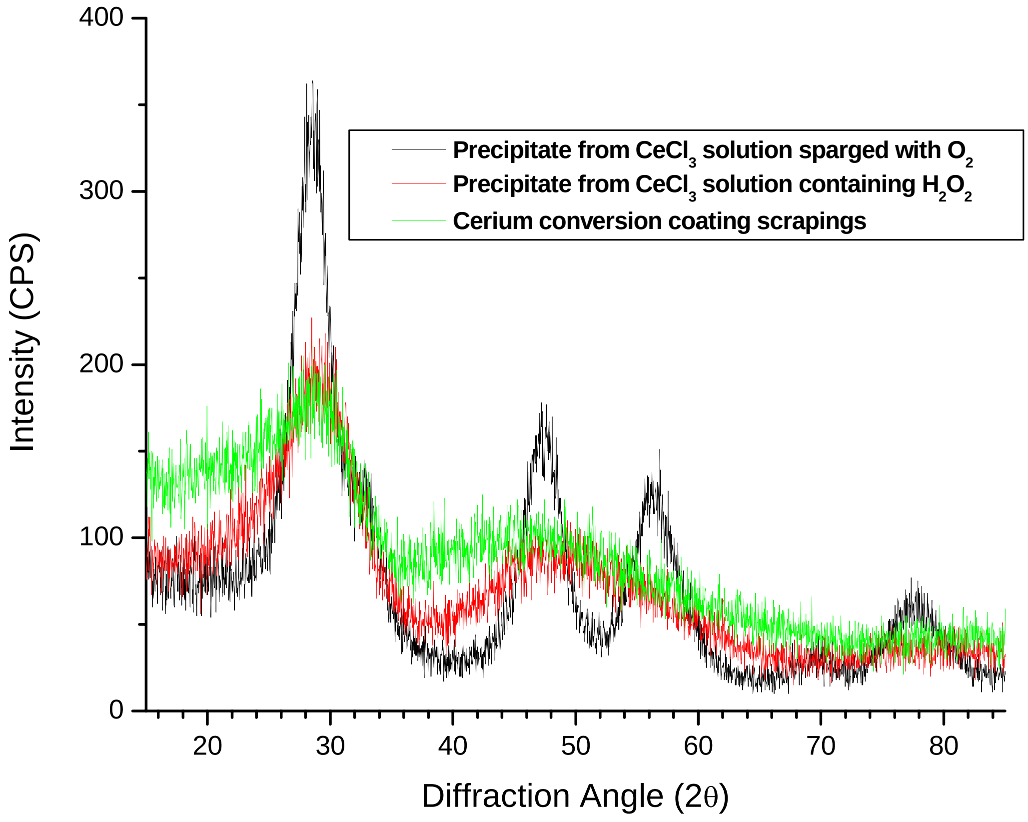

Figure 2. XRD Patterns of Precipitates and Conversion Coating

XRD patterns comparing the two precipitated powders to the cerium conversion coating scrapings.

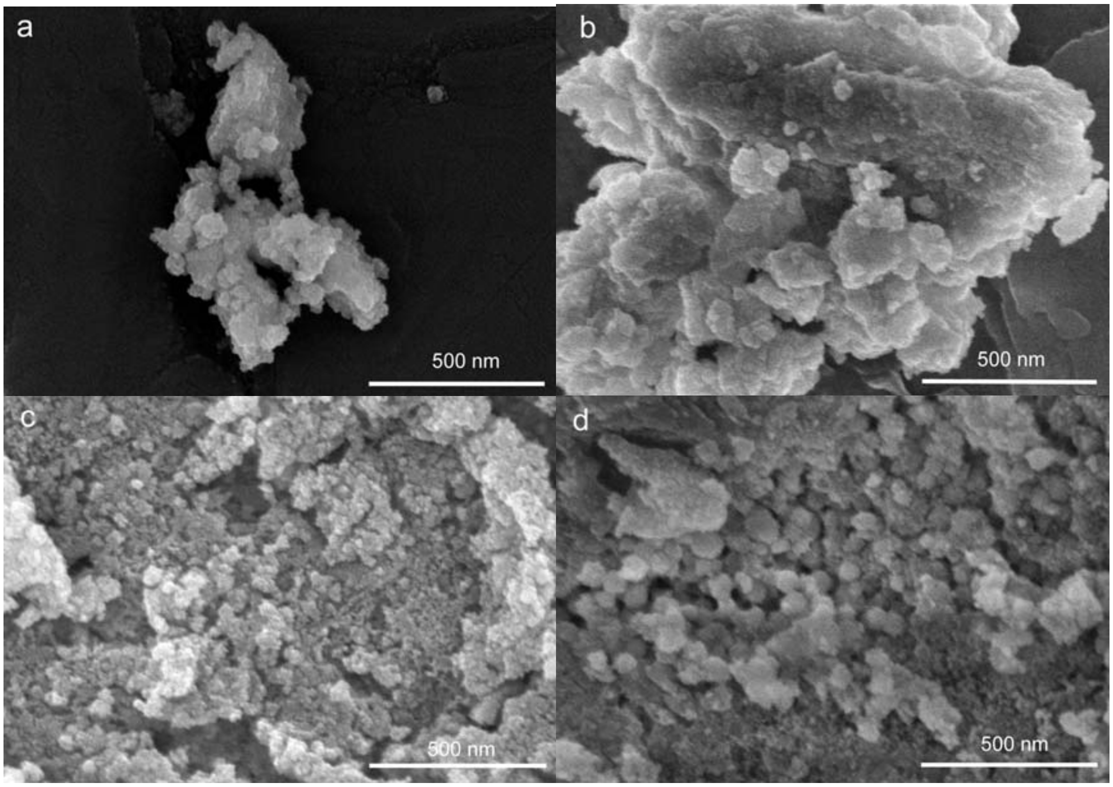

Figure 3. SEM Micrographs of Samples

SEM micrographs of a) cerium precipitate formed under oxygen sparging, b) cerium precipitate formed with hydrogen peroxide present, c) intact cerium conversion coating on 7075-T6, and d) cerium conversion coating after removal from substrate

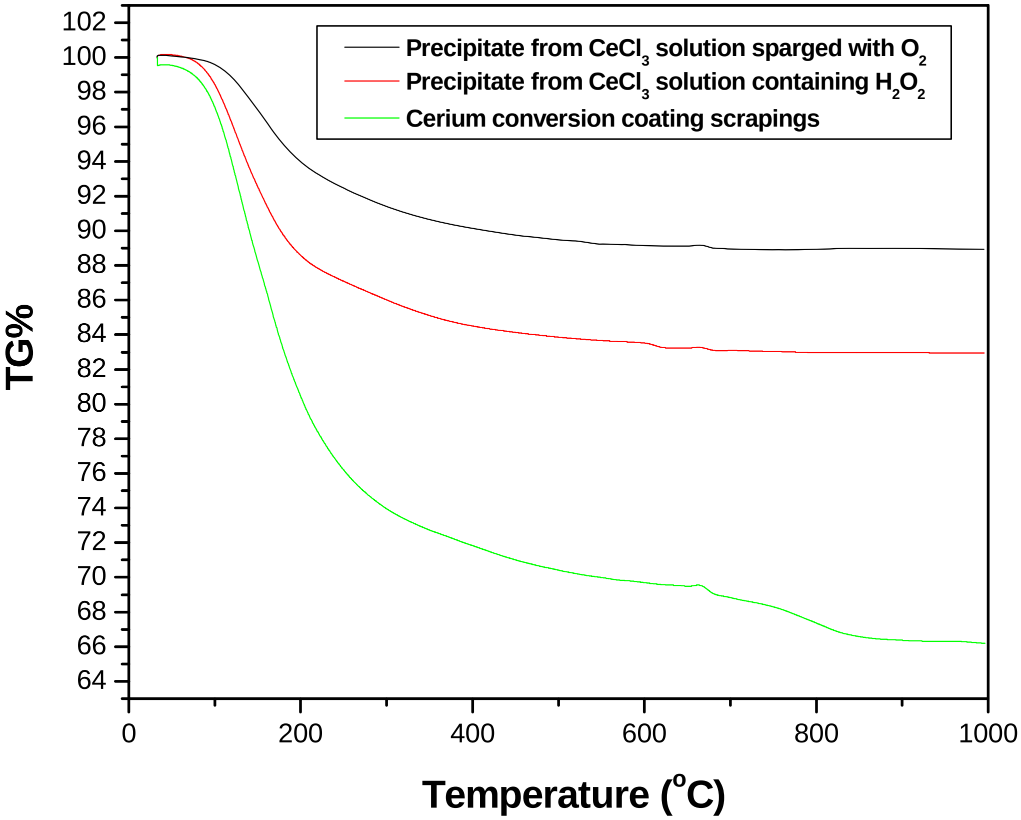

Figure 4. TGA Curves

TGA data showing weight loss upon heating for the three samples

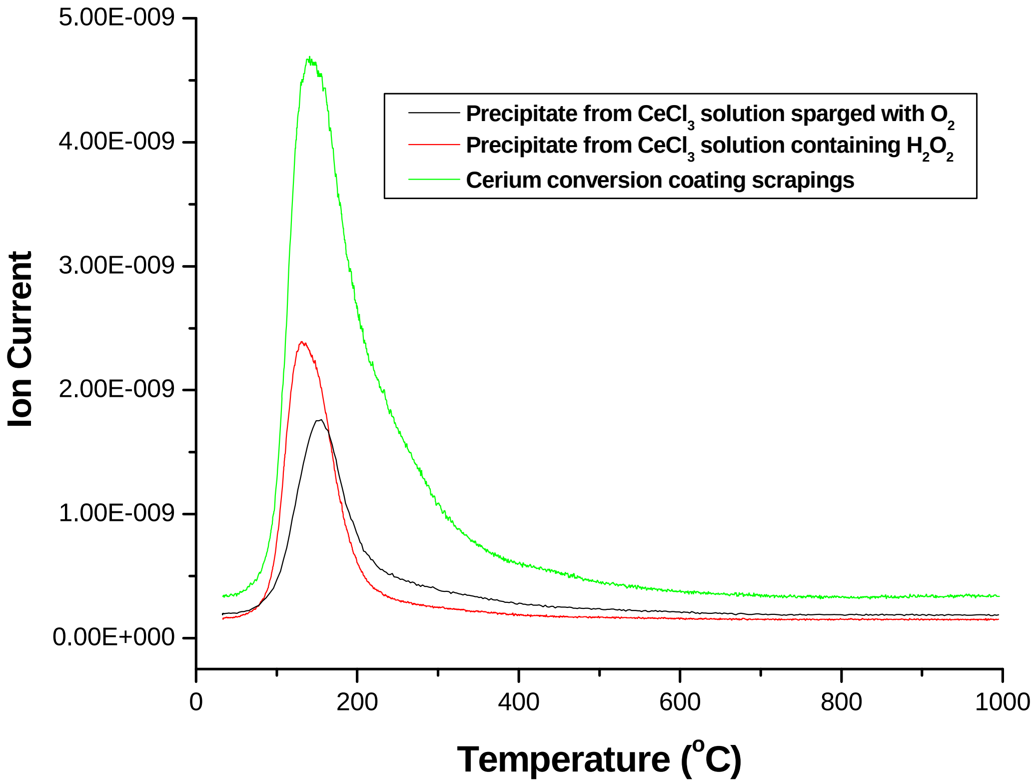

Figure 5. Signal for *m/z* =18 During TGA Analyses

Mass spectrometry data tracking the change in signal for *m/z* 18, which is assumed to be from water loss during heating. Heating rate was 10°C.

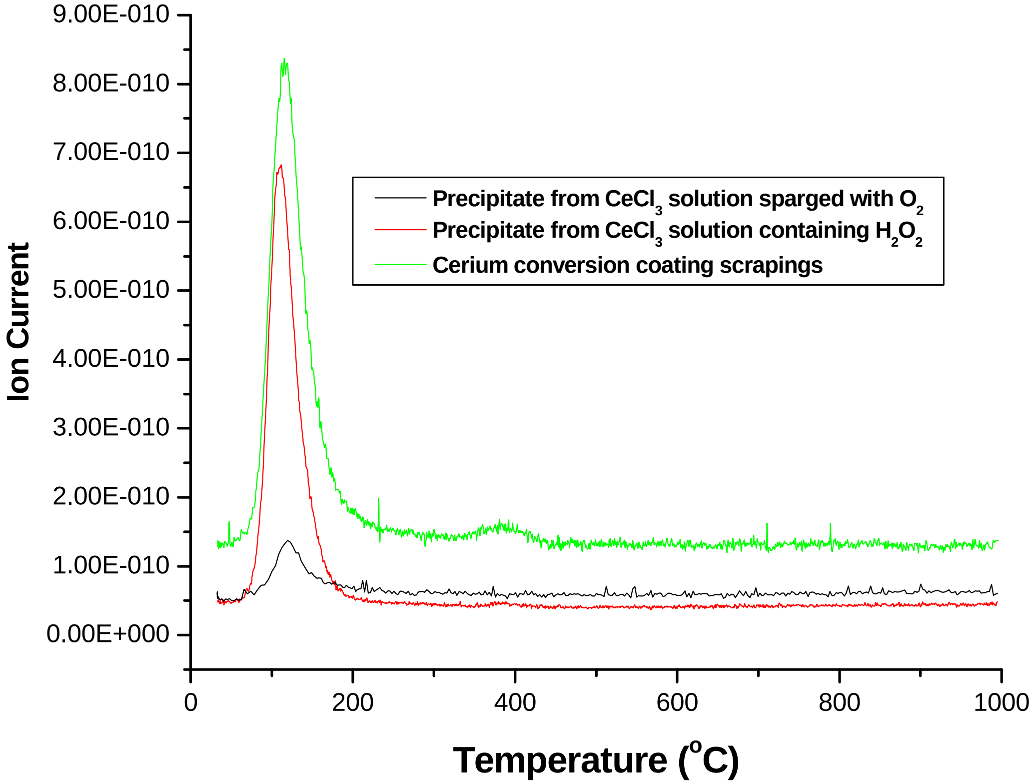

Figure 6. Signal for *m/z* 32 During TGA Analyses

Mass spectrometry data tracking the change in signal for *m/z* 32, which is assumed to be from oxygen evolved during heating. Heating rate was 10°C.