SURFACE AND INTERFACE ANALYSIS
Surf. Interface Anal. **27**, 273–282 (1999)

X-ray Photoelectron Spectroscopic Examinations of Beryllium Metal Surfaces Exposed to Chlorinated Solvents

J. C. Birkbeck,[1] N. L. Kuehler,[2] D. L. Williams[2] and W. E. Moddeman[3]*
[1] University of Dayton Material Science Engineering Department, Dayton, OH 45469, USA
[2] West Texas A&M University, Chemistry Department, Canyon, TX 79015, USA
[3] Mason & Hanger Corporation, Pantex Plant, Amarillo, TX 79120 USA

Beryllium has found applications in the nuclear industry as components in weapons and nuclear reactors, in the aerospace industry for special structural applications and in precision navigational instruments such as gyroscopes. The purity of the beryllium is known to have a large impact on its mechanical and chemical properties, including its corrosion resistance. Although chlorinated solvents have long been used to degrease and clean beryllium parts, not much has been reported about the potential effects of residual cleaning and processing agents left on the surface of beryllium. Recently, samples from some of the beryllium cladding that has been used in the nuclear industry have been found to contain corrosion promoters, e.g. chlorides. In addition, machined surfaces of more recent beryllium metal, e.g. S200 grades, were found to include chlorides. This paper involves using x-ray photoelectron spectroscopy to examine the effects of residual chlorinated solvents on beryllium under near-ambient conditions. Interpretation of the data concludes that these chlorinated solvents react with the beryllium metal surfaces to produce chlorides. Thermodynamic calculations are used to corroborate these results. A mechanism is proposed to explain the loss of the native protective oxide which exposes a reactive surface to the chlorine in the solvents to produce a chloride. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: XPS; Be; solvents

INTRODUCTION

For many years the major use of beryllium was as a precipitation hardening additive in copper alloys.[1,2,6] It was also used in precision navigational instruments, such as gyroscopes.[1,2,6] Then the nuclear industry realized the attractiveness of a strong lightweight metal with a high neutron scattering and low neutron capturing cross-section.[2] More recently, beryllium has become of interest to the aerospace industry due to its high strength/low weight ratio and its thermal conductivity.[3]

The corrosion performance of beryllium at elevated temperatures (>500 °C) and in aqueous environments has been examined and reported in the literature for over 30 years.[4–7] However, few articles can be found concerning the potential corrosion resistance of beryllium in less severe environments, say temperatures <100 °C and ambient humidity.[8,9] Although the purity of the metal is known to have a large impact on its mechanical and chemical properties, including its corrosion resistance, not much has been reported about the potential effects of residual cleaning or processing agents left on the surface of beryllium parts.[1,7] Chlorinated solvents were and still are, used extensively to degrease and clean beryllium parts. For example, samples from some of the beryllium cladding that is used in the nuclear industry have been found to contain corrosion promoters, e.g. chlorides (Cl^-).[10,11] In addition, machined surfaces of newer or more recent beryllium metal (grade S200D) were found to include Cl^-.[11] Beryllium normally forms a protective native oxide somewhat similar to that formed by aluminum. This oxide layer is generally insoluble in water and common solvents. It is soluble in concentrated acids and fuming based, whereas the chlorides of beryllium are very soluble in water as well as in ethyl alcohol, ethyl ether, chloroform and carbon disulfide.[12,13] Historically, beryllium metal surfaces containing chlorides have been shown to be particularly susceptible to pitting attack in humid environments.[1,4] Because chlorinated solvents have been used liberally in the nuclear industry, investigation of the solvent-exposed surfaces of beryllium is warranted.

This paper examines the effects of residual chlorinated solvents on beryllium under near-ambient conditions. A chlorinated surface of beryllium similar to those found on nuclear industry samples was produced in the laboratory and studied by x-ray photoelectron spectroscopy (XPS). In this study, beryllium metal coupons and powder were subjected to chlorinated solvents, such as those used during cleaning, processing or possibly machining of the metal surface prior to use in the nuclear industry. The data are interpreted that these chlorinated solvents react with the beryllium metal surfaces to produce chlorides. In humid environments, chlorinated surfaces have been found to be susceptible

---

* Correspondence to: W. E. Moddeman, Mason & Hanger Corporation, Pantex Plant, Amarillo, TX 79120, USA

CCC 0142–2421/99/040273–10 $17.50

Received 8 September 1998
Accepted 15 January 1999

Table 1. Chlorinated solvents

Solvent	Supplier	Grade	Impurities
1,1,1-Trichloroethane (TCA)	American Chemical Enterprises, Inc.	Technical per Federal Specification O-T-620 Issue C	$\geqslant$90% TCA by volume $\geqslant$2% all other halogens by volume Inhibitors Max. H_2O 100 ppm
1,1,2-Trichloroethylene (TCE)	Burdick & Jackson Laboratories, Inc.	Reagent grade	K-F H_2O 0.006% Residual 0.28 ppm
Carbon tetrachloride (CCl_4)	Matheson, Coleman & Bell	Spectroquality grade	99 + mol.% CCl_4 Max. H_2O 0.03%

to corrosion. Thermodynamic calculations will be used to corroborate these results. A mechanism will be proposed to explain the loss of the native protective oxide, which exposes a reactive surface to the chlorinated solvents. This exposure produces a surface chloride, which then promotes the attack of the beryllium in the presence of humidity.

EXPERIMENTAL

The standard for cleaning some nuclear components is vapor degreasing with a chlorinated solvent such as 1,1,1-trichloroethane (TCA) or possibly 1,1,2-trichloroethylene (TCE).[14] Occasionally, carbon tetrachloride (CCl_4) is also used during some processes. Table 1 lists the solvents used in this work; the suppliers, grade and major impurities are also given. Trichloroethane has an inhibitor package that performs the following functions: absorption of UV light, scavenging of acid and prevention of solvent reacting with bare metal.[15] Trichloroethylene has only trace amounts of these stabilizers, even in the ACS reagent grade.[15] These additives tend to be proprietary but often include butylene oxide, nitromethane and 1,3-dioxolane. The nitromethane prevents breakdown of chlorinated solvents by absorbing photons, especially from UV light. If chlorine-free radicals are formed, they react with any moisture in the solvent and form acids. The butylene oxide reacts with the acid to form an alcohol, thus protecting the metal from acid attack. The dioxolane is present to promote the formation of a protective oxide on reactive metals.

Owing to the safety factors involved when machining beryllium, beryllium (grade S200D) metal coupons ~1 cm in diameter and 2 mm thick were obtained from Lawrence Livermore National Laboratory, Livermore, CA for this work. The beryllium metal powder, 325 mesh, which corresponds to a particle size of 44 μm was procured from BrushWellman, Inc., Cleveland, OH. The compositions of the coupons and the powder are given in Table 2.

In all studies involving beryllium, the metal coupons were polished under distilled/deionized (DDI) water with Streurs waterproof silicon carbide paper (FEPA 4000). All coupons were then followed by an ultrasonic cleaning in the DDI water. The water used in these experiments was first distilled and then deionized so that its resistance was $\geqslant 15$ MΩ·cm (cole-Parmer, Instrument Co., Vernon Hills, IL). The coupons were allowed to air dry for ~4 h to form their native oxide and subsequently were exposed to vapors of either TCA or TCE. In vapor degreasing, the temperature of the metal parts is elevated. In the case of vapor degreasing or beryllium with TCA, it was determined that the beryllium reached a temperature of at least 50 °C. The treated metal coupons were then analyzed by XPS.

In order to ascertain the solubility, if any, of the native beryllium oxide in TCA, 1 g of beryllium metal powder was placed in a beaker and covered with 250 ml of TCA liquid. The temperature of the liquid and powder was raised to 50 °C and held for 20 min to simulate the interaction of the hot vapors that condense on the beryllium metal during vapor degreasing. (Vapor degreasing is done at various stages during the whole processing of the beryllium. Twenty minutes is roughly the maximum time for which the parts would be subjected to a chlorinated environment.) The solution was then allowed to cool. The beryllium metal powder was separated from the liquid in one of two ways. In the first experiment, the solution was centrifuged and 100 ml of the liquid was decanted very carefully. The experiment was repeated, but this time the solution was filtered through a 0.2 μm filter paper. Both of these solutions

Table 2. Composition of beryllium

Composition	S200D Beryllium Coupon impurities per specification (% ppm)	325 mesh beryllium powder impurities assay (wt.%)
Be	98.0	99.6
BeO	2.0	0.6
Al	0.16	0.03
Fe	0.13	0.07
Mg	0.18	<0.01
Si	0.08	0.02
C	0.15	0.03

were analyzed by inductively coupled plasma optical emission spectroscopy (ICP/ES) to determine the amount of beryllium in solution. The powdered beryllium samples were allowed to dry and then were analyzed by XPS.

Next, the DDI water-polished coupons were polished under either TCA or CCl_4. This experiment was performed to examine the possible reaction of beryllium metal to chlorine containing solvents, such as would occur if the beryllium was processed, e.g. scraped, scratched or machined, in the presence of these or similar chlorine-containing coolants or solvents. As a continuation of this study, two beryllium coupons were submerged in the liquid and scraped with the edge of a hardened steel screwdriver. The sample was removed from the solvent and the TCA was allowed to evaporate, which required just a few seconds. Although gouges and uneven scratch marks could be seen in the metal surface at low magnification, only a small portion of the beryllium was actually removed by scraping, as evidenced by microscopic inspection of the surface. The solvent-polished and the solvent-scraped samples were then analyzed by XPS.

Finally, the DDI water-polished beryllium coupons were vapor degreased in TCA and then rinsed with copious amounts of DDI water. This was followed by a light swipe with a Kimwipe saturated with DDI water. This experiment was done to determine if the surface chlorides could be removed by a DDI water rinse.

A Kratos Analytical AXIS HSi XPS spectrometer was used to analyze the chemistry of the metal surfaces. The x-ray source used in these XPS measurements was an aluminum anode. A quartz crystal of Johann geometry focused monochromatic aluminum Kα photons of 1486.6 eV onto the samples. Approximately 1 h per sample was required to accumulate the low-resolution scans. The Cl 2p and the Be 1s high-resolution scans required counting times of 2–5 h for chlorine and 0.5–1 h for the beryllium.

A SpectroFlame Model FTM-08 inductively coupled plasma optical emission spectrometer manufactured by Spectro-Analytical Instruments was used to analyze the TCA solutions that were decanted or filtered from the beryllium powder. The solvent solutions were dried at 120 °C under a slight vacuum. The residues were digested in a nitric acid matrix to eliminate any organic residues and then diluted with DDI water. The samples were pumped into a nebulizer and then into the 2000 °C plasma for analysis.

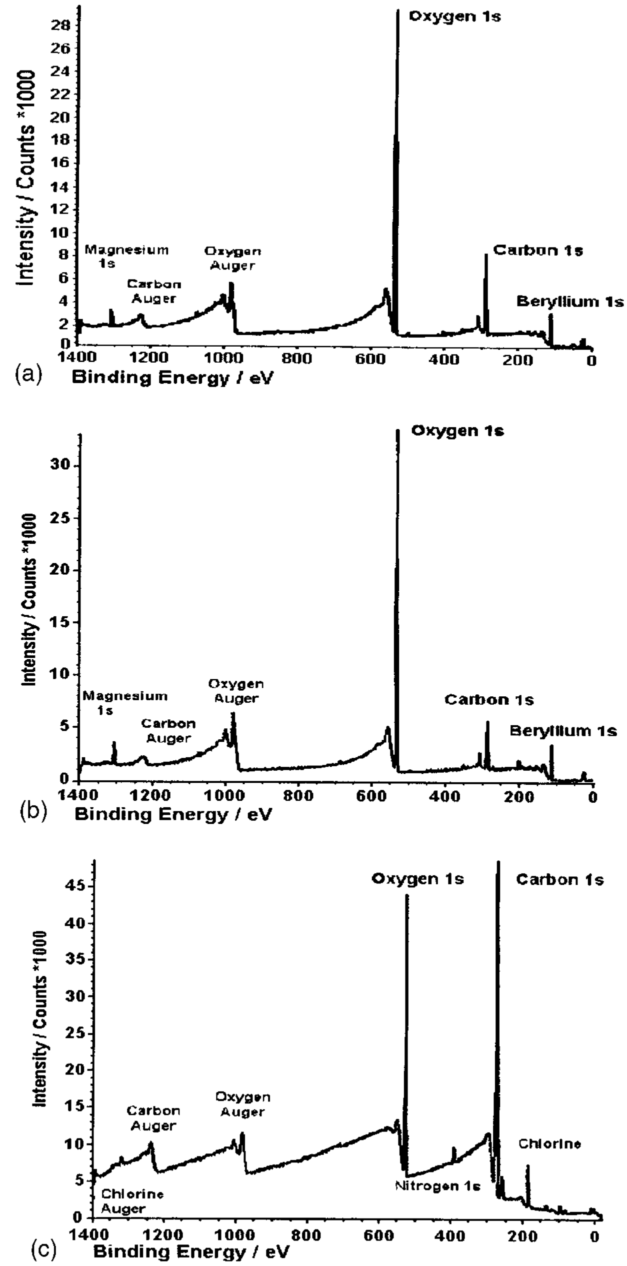

Figure 1. The XPS survey scans of beryllium metal coupons: (a) DDI water-polished; (b) DDI water-polished followed by vapor degreasing in TCA; (c) DDI water-polished followed by vapor degreasing in TCE.

RESULTS AND DISCUSSION

Exposing beryllium metal to vapor degreasing solvents

Low-resolution XPS scans. Figure 1 shows representative low-resolution XPS survey scans in the range 0–1400 eV binding energy of three different beryllium metal coupon surfaces. All three coupons were DDI water-polished. The first coupon was left at this stage [Fig. 1(a)]. The second coupon was then exposed to TCA vapors [Fig. 1(b)] and the third coupon was exposed to TCE vapors [Fig. 1(c)]. The average atomic percentages of the major elements are summarized in Table 3; these are meant to be only semi-quantitative values and do not imply absolute atomic concentrations. The sample that was DDI water-polished only shows a possible trace of chlorine (<0.03), whereas the DDI water-polished samples that were subsequently exposed to the TCA and TCE vapors revealed chlorine signals of 0.5 and 4.8 at.%, respectively. These data show that both solvents leave the beryllium surface chlorinated, with TCE leaving behind a larger chloride concentration than TCA.

Figure 2 shows expanded portions (0–280 eV) of the same low-resolution XPS scans of Fig. 1 to allow easier viewing of the XPS Cl 2s and 2p signals at ~280 and ~200 eV, respectively. Also seen in these expanded

Table 3. Summary of semi-quantitative data taken from low-resolution XPS scans

Sample/element	XPS analyzed sub-level	DDI water-polished only	DDI polished and vapor degreased in TCA	DDI polished/vapor degreased in TCE (at.%)	DDI polished/scraped in TCA/H_2O rinsed (at.%)
Number of runs		15	5	1	2
Carbon	1s	19.	13.	67.	12.
Oxygen	1s	31.	31.	20.	32.
Beryllium	1s	49.	54.	7.6	52.
Chlorine	2p	<0.03	0.5	4.8	0.2

scans are signals from small amounts of other elements: phosphorus, silicon, magnesium, aluminum, sodium and sulfur. The magnesium and aluminum are impurities in the beryllium (Table 2). The silicon is from the silicon carbide used in polishing. The others are trace amounts of contaminants left after polishing.

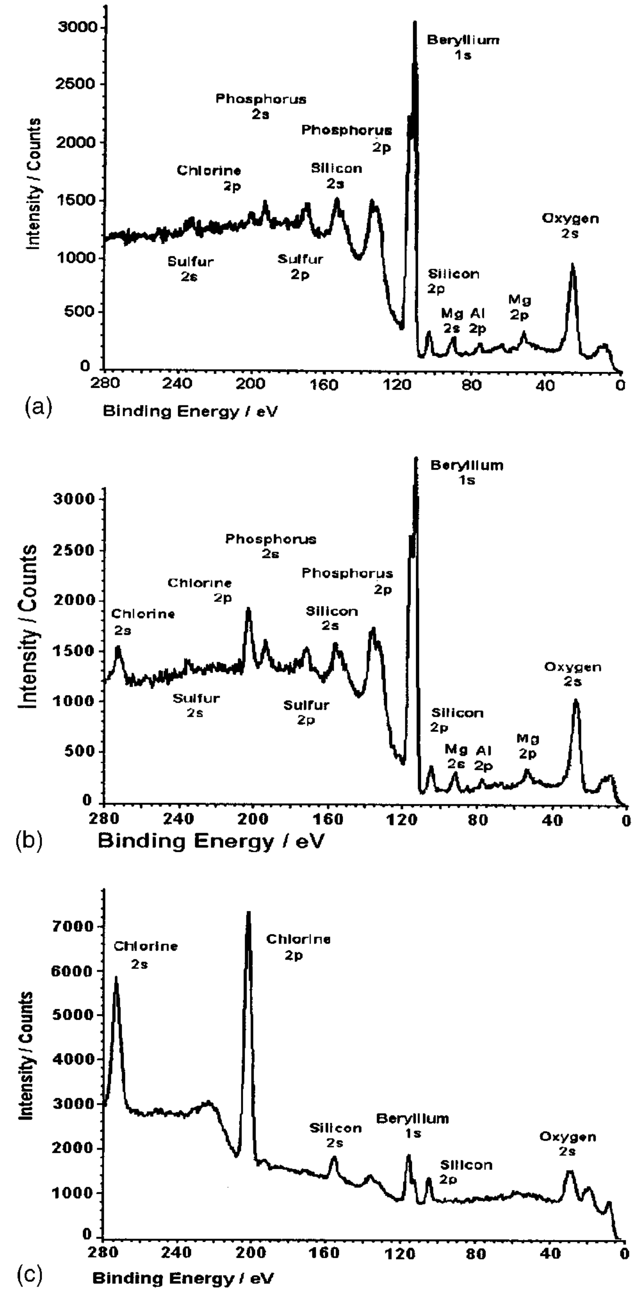

Figure 2. Expanded XPS survey scans of beryllium metal coupons: (a) DDI water-polished; (b) DDI water-polished followed by vapor degreasing in TCA; (c) DDI water-polished followed by vapor degreasing in TCE.

High-resolution XPS scans. Figures 3 and 4 are representative high-resolution scans of Cl 2p and Be 1s on the above three beryllium metal coupons: the DDI water-polished coupons (a) and the DDI water-polished coupons followed by vapor degreasing in TCA (b) or TCE (c).

Chlorine 2p spectra. The Cl 2p scan recorded on the DDI water-polished coupon [Fig. 3(a)] shows no detectable chlorine. (Peaks were force fitted into the noise level of the spectrum.) The samples that were DDI water-polished followed by vapor degreasing [Figs 3(b) and 3(c)] show much higher chlorine levels. A closer investigation of the Cl 2p spectra from the vapor-degreased samples reveals the presence of a broad structure that was deconvoluted into four different peaks. The four peaks are two sets of doublets. A doublet arises from the spin-orbit splitting that occurs during photoionization of the 2p atomic sub-level of chlorine and is inherent in the spectra.[16] The two peaks of the doublet are: Cl $2p_{3/2}$ and Cl $2p_{1/2}$, which are separated by 1.6 eV and are present in a 2:1 ratio. The binding energies of the four peaks are summarized in Table 4. All binding energy data are referenced to the residual carbon peak, which was observed in the spectra at 284.9 ± 0.1 eV.

The data are interpreted as chlorine being present on the surface of the beryllium in two different chemical bonding states; the first, a bound organic chloro-containing compound whose Cl $2p_{3/2}$ binding energy was measured to be 200.5 eV; and the second, an inorganic chloride whose Cl $2p_{3/2}$ binding energy was determined to be 198.3 eV. (The corresponding Cl $2p_{1/2}$ binding energies for the two states were seen at 202.1 and 199.9 eV, respectively.) These assignments agree with literature data.[16] Thus, the TCA and TCE vapors have reacted with the beryllium metal to produce a surface that contains both organic and inorganic chlorine, the latter being susceptible to attack by water and known to promote corrosion.[4–7]

Beryllium 1s spectra. The Be 1s high-resolution scans in Fig. 4 show two distinct peaks: one due to beryllium metal (Be^0) found at binding energies between 110.8 and 110.6 eV; and the second due to beryllium in a + 2 oxidation state (Be^{II}) observed at binding energies between 113.5 and 114.2 eV. The beryllium data are also summarized in Table 4.

The Be^{II} state of the DDI water-polished coupons was measured at 113.5 eV and its metal state (Be^0) at 110.8 eV. The total intensity of the beryllium signal was

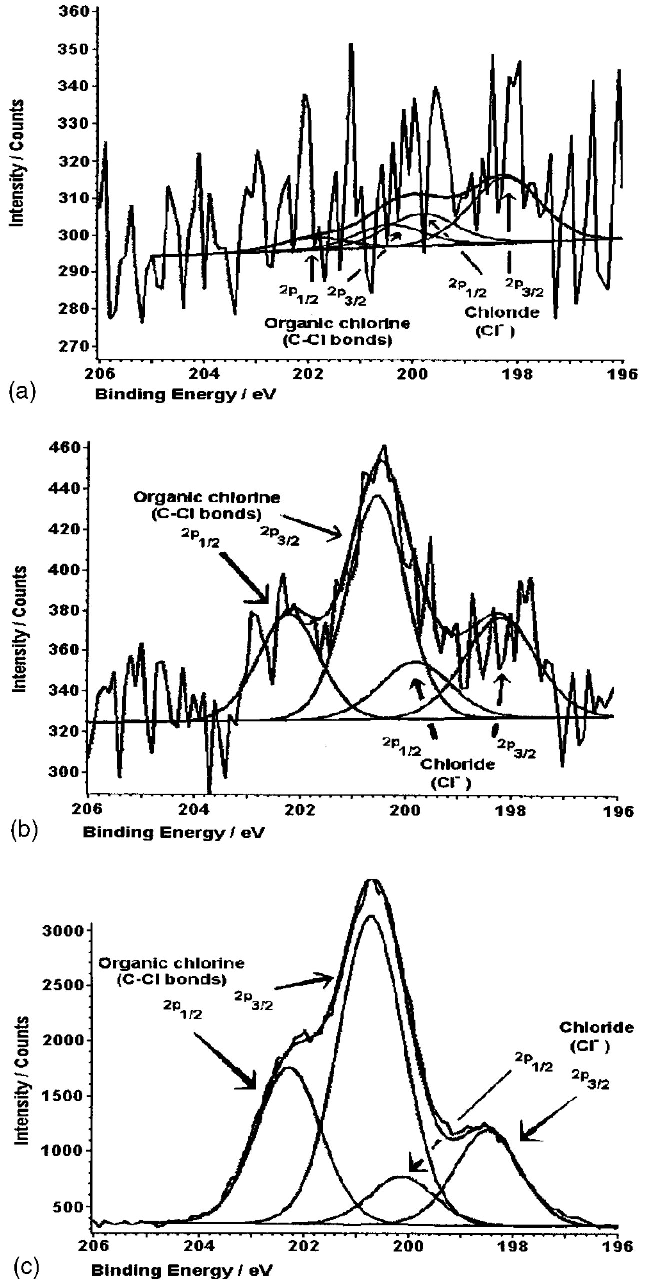

Figure 3. High-resolution XPS Cl 2p spectra of beryllium metal coupons: (a) DDI water-polished (peaks were force fitted); (b) DDI water-polished followed by vapor degreasing in TCA; (c) DDI water-polished followed by vapor degreasing in TCE.

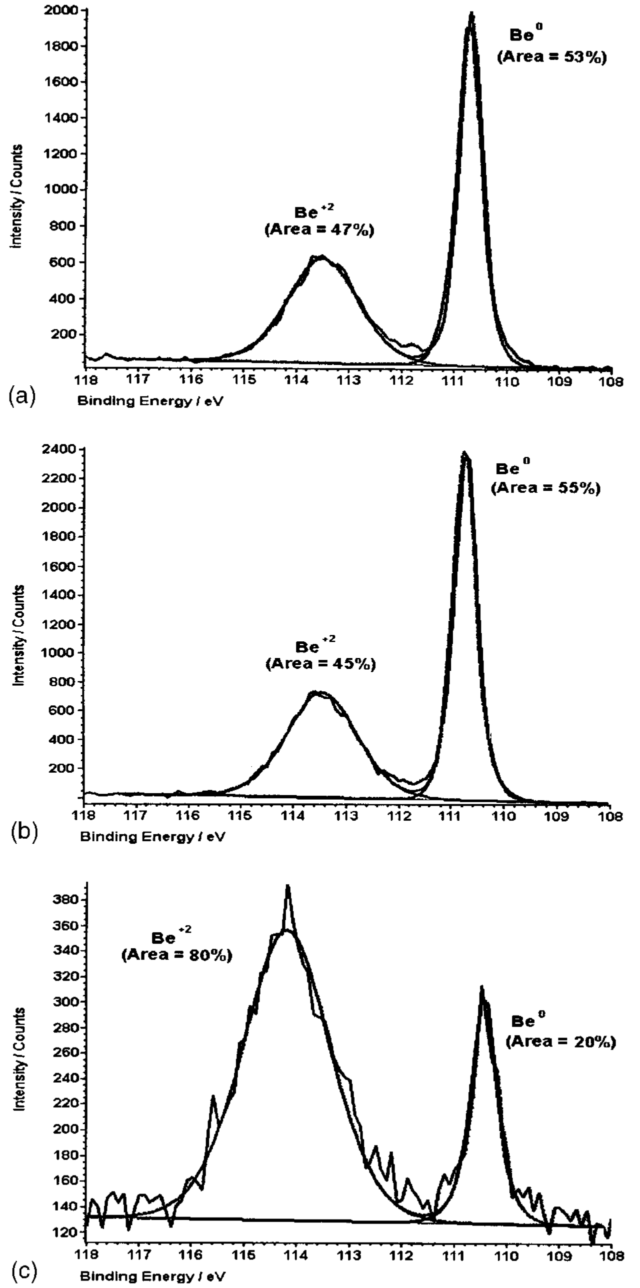

Figure 4. High-resolution XPS Be 1s spectra of beryllium metal coupons: (a) DDI water-polished; (b) DDI water-polished followed by vapor degreasing in TCA; (c) DDI water-polished followed by vapor degreasing in TCE.

determined to be 49 at.%, and the ratio of Be^{II} state to Be^0 was 1.2. This supports the removal of some of the carbonaceous material from the surface. No detectable change in the positions of the two peaks was found following exposure to TCA vapors. However, a small and reproducible increase in the total intensity of the beryllium signal (~6 at.%) was noted for the TCA samples. The increase in the total beryllium signal was attributed to the beryllium surface having less residual organic compounds following vapor degreasing in TCA. In other words, the TCA vapor degreasing technique is removing, as expected, some of the organic compounds from the beryllium metal surface.

A dramatic change is noted in the intensity and position of the Be 1s peaks when a DDI water-polished beryllium surface is exposed to TCE vapors. First, the total intensity of the beryllium signal has been reduced to 7.6%, and the ratio of the intensity of the Be^{II}/Be^0 peaks has increased to 4. These results are interpreted as being due to the formation of new compounds on the surface of the metal during vapor degreasing with TCE. This new surface consists of both organic and inorganic compounds, which reduce the intensity of the characteristic photoelectrons from the Be 1s metal substrate. Second, the binding energy difference between Be^{II} and Be^0 increases from 2.7 eV for the DDI water-polished sample to 3.6 eV for the sample exposed to TCE vapors. The broad structure of the Be^{II} state is most likely due to more than one chemical compound on the surface of the Be metal. These possible new compounds could

Table 4. Summary of high-resolution Cl 2p and Be 1s XPS scans of beryllium metal coupons that were DDI water-polished and DDI water-polished followed by vapor degreasing in, or scraping under, TCA or TCE

	Chemical state assignment	Sample treatment	Binding energy (eV)	Intensity (at.%)
Cl $2p_{3/2}$	Organic	(a) Water-polished	(200.5)[a]	< 0.02
	(C–Cl bond)	(b) TCA vapor degreased	200.3	0.25
		(c) TCE degreased	200.3	2.40
		(d) TCA scraped	(200.3)[a]	<0.02
		(e) TCA scraped, H_2O rinse	200.3	0.05
Cl $2p_{1/2}$	Organic	(a) Water-polished	(202.1)[a]	<0.01
	(C–Cl bond)	(b) TCA	201.9	0.12
		(c) TCE	201.7	1.20
		(d) TCA scraped	(201.8)[a]	–
		(e) TCA scraped, H_2O rinse	201.9	0.02
Cl $2p_{3/2}$	Inorganic chloride	(a) Water-polished	(198.3)[a]	<0.02
		(b) TCA	198.3	0.08
		(c) TCE	198.3	0.74
		(d) TCA scraped	198.3	1.60
		(e) TCA scraped, H_2O rinse	198.2	0.08
Cl $2p_{1/2}$	Inorganic chloride	(a) Water-polished	(199.9)[a]	<0.01
		(b) TCA	199.9	0.04
		(c) TCE	199.8	0.37
		(d) TCA scraped	199.9	0.80
		(e) TCA scraped, H_2O rinse	199.8	0.04
Be 1s	Be^{II} oxidized state	(a) Water-polished	113.5	27.0
		(b) TCA	113.5	30.0
		(c) TCE	114.2	6.0
		(d) TCA scraped	113.6	36.0
		(e) TCA scraped, H_2O rinse	113.6	30.0
Be 1s	Be^0 metal	(a) Water-polished	110.8	22.0
		(b) TCA	110.8	25.0
		(c) TCE	110.6	1.5
		(d) TCA scraped	110.6	16.0
		(e) TCA scraped, H_2O rinse	110.5	22.0

[a] Peaks fitted into spectrum noise.

contain Be–Cl bonds from Be_xO_yCl and Be–C bonds possibly from Be_x–CCl_3-type structures.

Beryllium metal powder exposed to liquid TCA at 50 °C

Each of the solutions separated from the beryllium metal powder after heating in TCA at 50 °C for 20 min were analyzed by ICP/ES for the amount of beryllium in solution. An average of 1 μg ml^{-1} beryllium was detected in each of the two liquid samples. Obviously some of the beryllium from the original oxide layer is dissolving in the liquid TCA. However, XPS analysis of the exposed and dried powder surfaces showed no surface chloride, but revealed a comparable oxide thickness to the unexposed powder (Fig. 5). This is in direct contrast to the results obtained for the vapor-degreased coupons mentioned above. An explanation for this difference in the beryllium surface chemistry of the metal exposed to vapor *vs.* metal exposed to liquid is proposed in the following paragraphs.

The boiling point of the butylene oxide (63 °C) is less than the boiling point of TCA (74 °C). In the liquid at 50 °C, it is hypothesized that the butylene oxide evaporates fairly early in the experiment, leaving the TCA unprotected for acid formation. However, the dioxolane (boiling point 105 °C) is still present in the TCA liquid and continues to protect the metal by replenishing the oxide. In the liquid there are two competing reactions: the passivation process, which replenishes the oxide, appears to proceed a little faster than the attack by the acid, which results in no chloride. This conclusion is reinforced by the fact that the acid must form before it can react, whereas the dioxolane is already present in the liquid.

In vapor degreasing, the butylene oxide again evaporates early in the process. It is likely during this early time that the butylene oxide reacts with any of the acid that forms in the vapors, thus protecting the metal. However, after it is evaporated, the metal is susceptible to the acid attack. Note that the dioxolane concentration in the vapors is less than the dioxolane in the liquid due to its higher boiling point or lower vapor pressure. Hence, the dioxolane is in lower concentration in the TCA rich vapors and cannot re-passivate the metal efficiently. Therefore, unlike the powder in the solution, there are chlorides formed on the surface of vapor-degreased beryllium metal.

Beryllium scraped under liquid TCA and polished under CCl_4 or TCA

Beryllium metal was exposed to two different chlorinated solvents: TCA and CCl_4. These studies were performed to examine the possible reaction of beryllium

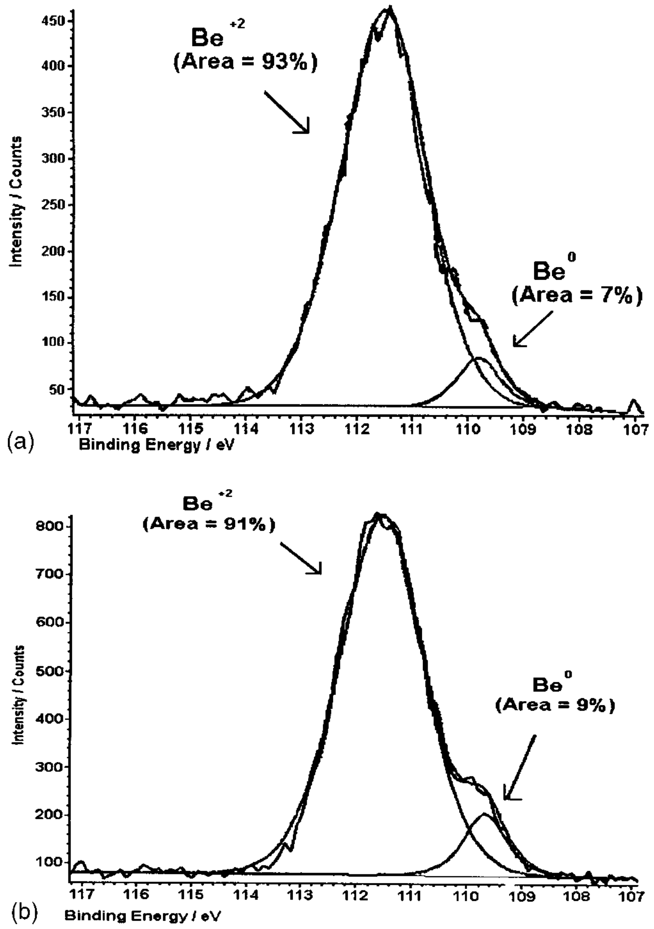

Figure 5. High-resolution XPS Be 1s spectra of beryllium metal powder: (a) untreated beryllium metal powder; (b) beryllium metal powder heated in TCA at 50 °C for 20 min.

metal with these chlorine-containing solvents, as would occur if beryllium was processed, scraped, scratched or possibly machined in the presence of these or similar chlorine-containing coolants or solvents.

Scraping beryllium metal under liquid TCA. In this experiment, the beryllium metal was submerged in the liquid and scraped with the edge of a hardened steel screwdriver. Figures 6(a) and 6(b) illustrate the presence of Cl 2p and 2s signals in the survey scan. Figures 6(c) and 6(d) are the high-resolution Cl 2p and Be 1s scans, respectively. These scans show that chlorine is present primarily as Cl^-, and the Be^{II} state has increased in thickness compared to the DDI water-polished sample on the surface of the metal. These results show that Be metal is reacting with TCA liquid, forming a surface Cl^-.

Polishing beryllium metal under liquid CCl_4. In this experiment, a DDI water-polished beryllium coupon was repolished under liquid CCl_4 with 4000 grit Streurs silicon carbide paper. After polishing, the sample was rinsed with CCl_4 liquid, which was allowed to evaporate. An inorganic chloride was again observed in both the Be and Cl XPS spectra, consistent with the sample scraped under TCA mentioned above.

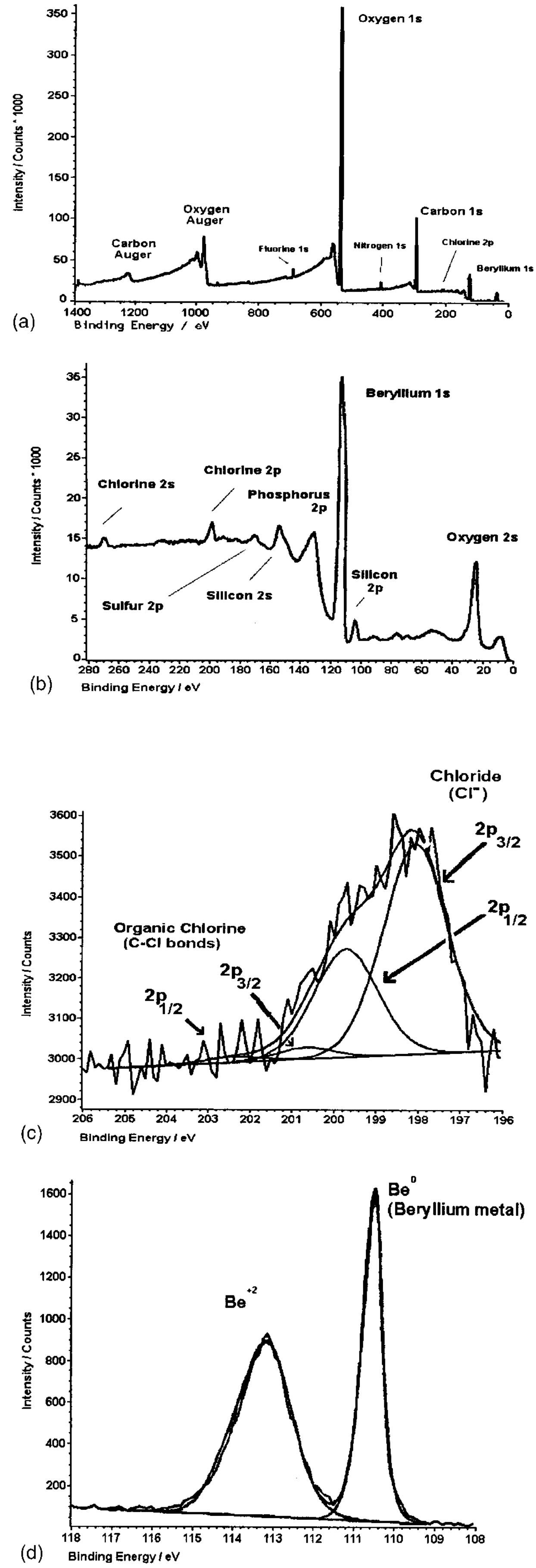

Figure 6. Low-resolution XPS scans (a, b) and high-resolution XPS Cl 2p (c) and Be 1s (d) of beryllium metal coupon scraped under TCA.

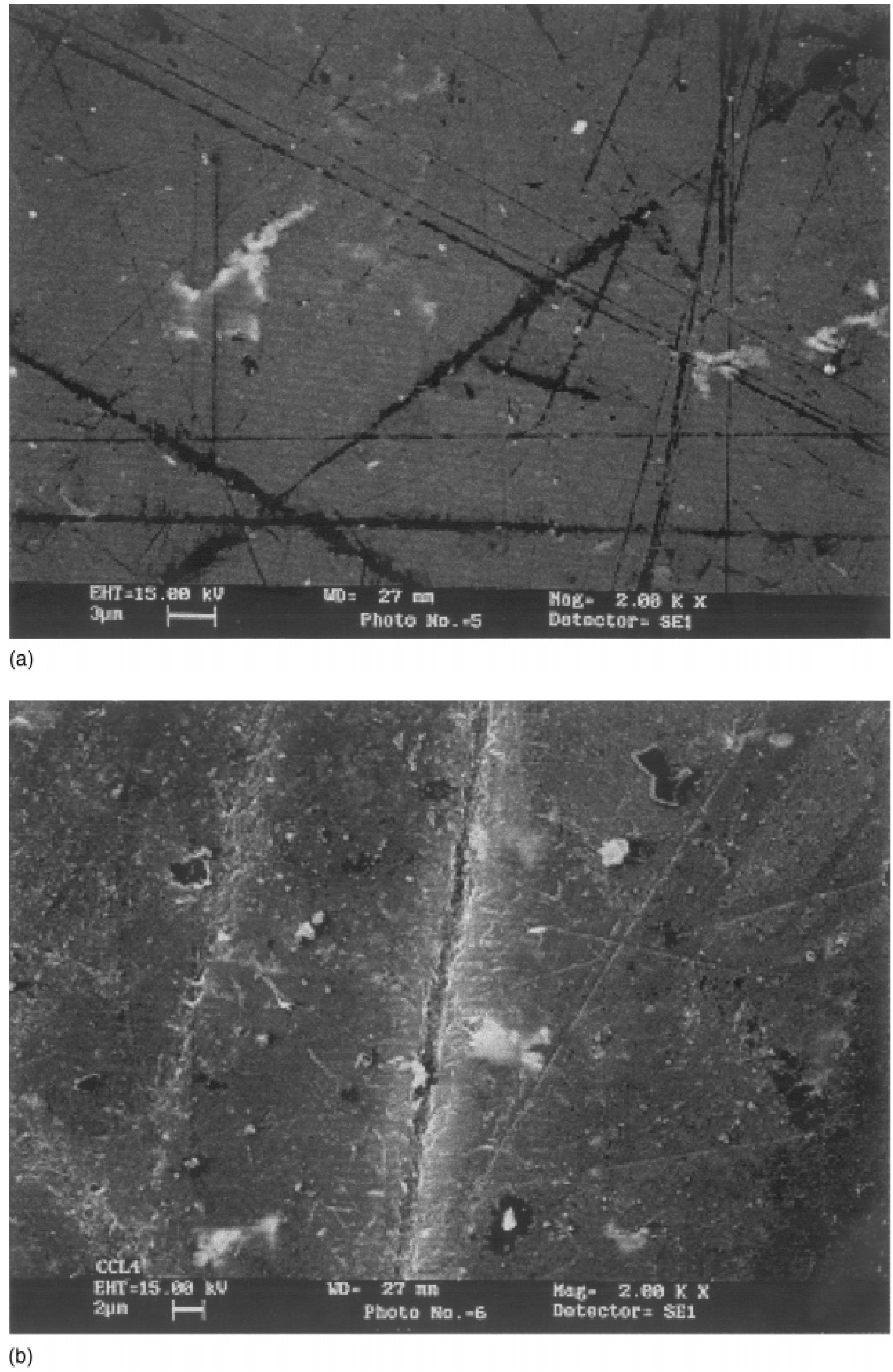

Figure 7. Scanning electron of DDI water-polished beryllium coupons: (a) H_2O polished and exposed to H_2O vapors; (b) polished under CCl_4 and exposed to H_2O vapors.

Following XPS analysis, the above sample polished under CCl_4 was suspended in H_2O vapors for 1 week. These vapors were generated by heating water to ~60 °C. Scanning electron photomicrographs were taken on this sample following the exposure. The picture [Fig. 7(b)] shows attack of the metal surface occurring along the polishing marks. The XPS results revealed the beryllium surface to be a thickened beryllium oxide with no chloride in evidence. The reaction of the metal with the H_2O vapors formed the additional oxide following dissolution of the chloride. This leads to the loss of the passive film, resulting in oxidation and general corrosion of the metal surface. At the same time, a sample that was water-polished only was exposed to the same humid environment. The SEM micrograph [Fig. 7(a)] of this sample reveals less attack along the polishing marks, and the corresponding XPS results show a thinner oxide than the CCl_4.

Scraping under TCA followed by rinsing in distilled water

The corresponding low- [Figs 8(a) and 8(b)] and high-resolution [Figs 8(c) and 8(d)] scans for a sample that received the following treatment are shown below. The treatment included using a DDI water-polished scraping under TCA coupon. This coupon was then rinsed with copious amounts of DDI water and finally physically wiped with a Kimwipe saturated with DDI water.

The results that have been incorporated into Table 4 showed that the XPS signal from the Cl 2p level was reduced. Beryllium chloride is water soluble, and the data support these findings. The XPS Cl 2p signal is reduced by better than 80%. From a practical point of view, these results suggest that if TCA is to be used as a solvent, it must be followed by a DDI water rinse. This experiment was repeated using a coupon scraped under liquid TCA followed by rinsing with copious amounts of DDI water. The result agreed with the vapor-degreased, water-rinsed study. In this latter experiment, the chloride signal was reduced by better than 50%.

Thermodynamic calculations

Scraping or polishing a beryllium metal coupon under TCA and CCl_4 liquid resulted in the formation of an inorganic chloride [see Fig. 3(d)], whereas vapor degreasing with TCA or TCE produces a mixture of both inorganic chloride and chloro-organic compounds on the surface of the metal [see Fig. 3(b) or 3(c)]. Thermodynamic calculations can be used to support inorganic chloride formation. An abrasive action caused by accidental scratching or by a machining operation removes the surface oxide and exposes the bare metal. Under this abrasive condition, the Be–Be bonds of the metal could react with C–Cl bonds of the chlorinated solvent to produce a Be–Cl bond; a possible general

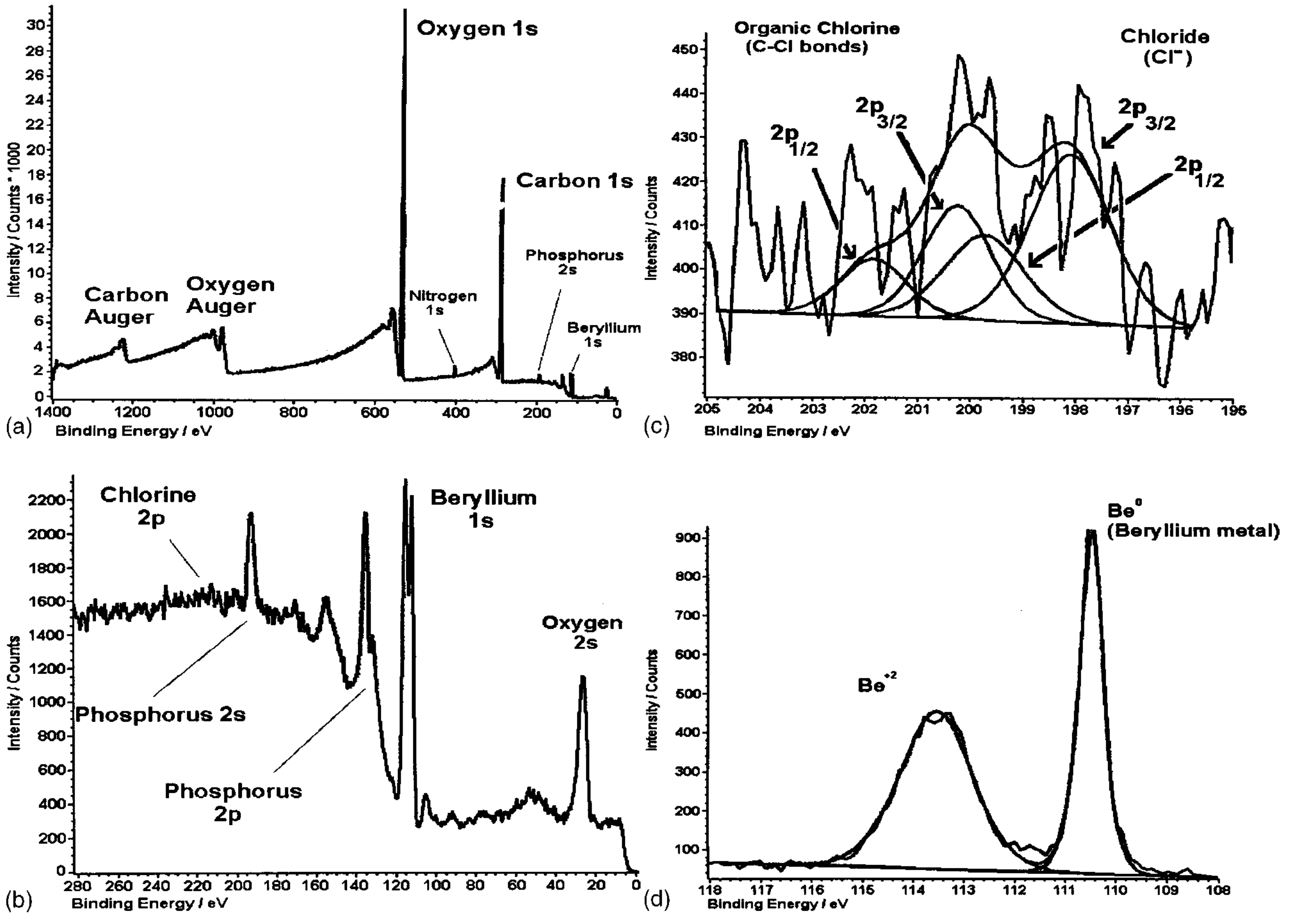

Figure 8. Low-resolution XPS scans (a, b) and high-resolution XPS Cl 2p (c) and Be 1s (d) of beryllium metal coupon scraped under TCA, followed by a DDI water rinse and wipe.

reaction would be

$$\text{Be–Be} + \text{C–Cl} \rightarrow \text{Be–C} + \text{Be–Cl}$$

The bond energies (calculated from Hess' Law) for these species are 2.81, 80.0, 143 and 91.7 kcal mol^{-1}, respectively.[12] Thus, the reaction is very thermodynamically favorable at room temperature, with a large negative enthalpy of reaction (-152 kcal). Although the exact stoichiometry is not known, possible reactions of C–Cl with a passivated surface of beryllium that contains Be–O bonds to form Be–Cl and C–O bonds will have a positive enthalpy (~ 10.9 kcal).[17] Therefore, the C–Cl bond is less likely to react with Be–O bonds of a passivated surface than to the metal–metal bonds of bare beryllium metal. These results support the XPS data where physically removing the beryllium oxide by scraping and immediately exposing this surface to a chlorinated solvent, such as TCA, resulted in the formation of a surface chloride. In the case of vapor degreasing, the passivating oxide must first be altered, i.e. dissolved, before a reduced state of the metal surface is available for reaction and surface Cl^- formation can occur.

CONCLUSIONS

The effects of exposing beryllium metal to chlorinated solvents have been examined. Results from both liquid and gaseous phase exposures revealed the formation of chlorides on the surface of the beryllium metal coupons. The liquid exposure involved polishing and scraping. In scraping or polishing of the metal under a chlorinated liquid, the oxide is physically removed. This exposes fresh metal to the organochlorine environment, resulting in chloride formation. The gas exposure was accomplished through a modified vapor degreasing process consistent with that used in the nuclear industry. In vapor degreasing, the mechanism of chloride production was shown to be dissolution of the oxide, followed by reaction of the solvent with a reactive surface. It was shown that these chlorides could be minimized by rinsing with copious amounts of DDI water followed by a light wipe with a Kimwipe soaked with DDI water. The recommendation of the authors is that when chlorinated solvents are employed in the processing of reactive metals such as beryllium, one needs to follow the exposure with a DDI water rinse and/or wipe. These results were supported by thermodynamic calculations based on bond energies.

Acknowledgements

The authors would like to acknowledge the support of J. J. Oldani for providing the S200D beryllium coupon samples and both J. J. Oldani and J. D. LeMay of Lawrence Livermore National Laboratory, Livermore, CA, for encouragement in these studies. The authors also acknowledge the support of D. E. Dombrowski, Technical Marketing Manager of Beryllium, BrushWellman, Inc. for providing the chlorine assay in various grades of beryllium and R. P. Garner, Quality Control, BrushWellman, Inc., for providing the chemical assay of beryllium powder.

J.C.B. and N.L.K. were supported by the Mason & Hanger Corporation, Plantex Plant, Amarillo, Texas and W. E. M. was supported by the Department of Energy, contract no. DE-AC04-91AL-65030. In addition, the authors would like to thank D. Kolman, S. Lillard and G. Carlson of Los Alamos National Laboratory for their support.

REFERENCES

1. W. G. Denhard, *MIT Report E-1658*. Massachusetts Institute of Technology, Boston, MA (1964).
2. H. P. Godard, W. B. Jepson, M. R. Bothwell and R. L. Kane, in *The Corrosion of Light Metals*, p. 221. Wiley, New York (1967).
3. W. Hodge, *Battelle Tech. Rev.* **13**, 12 (1964).
4. A. J. Stonehouse and W. W. Beaver, *Mater. Protect.* **4**, 24 (1965).
5. D. W. Alymore, S. J. Gregg and W. B. Jepson, *J. Nucl. Mater.* *3* **2**, 190 (1961).
6. L. L. Shreir, *Corrosion*, Vol. 1, Newnes–Butterworth, London (1963).
7. J. J. Mueller and D. R. Adolphson, in *Beryllium Science and Technology*, Vol. 2, edited by D. R. Floyd and J. N. Lowe. Plenum Press, New York (1979).
8. J. L. English, in *The Metal Beryllium*, edited by D. W. White, Jr. and J. E. Burke, Chapt. IX. American Society for Metals, Cleveland, OH (1955).
9. M. A. Hill, D. P. Butt and R. S. Lillard, *J. Electrochem. Soc.* **145**, 2799 (1998).
10. W. E. Modderman, J. C. Birkbeck and K. C. Coleman, *Chlorides Observed on Clad Metal Beryllium*, Beryllium Corrosion Meeting Report, LANL (March 1997).
11. W. E. Moddeman and J. C. Birkbeck, *Surface Analysis on Processed Beryllium Metal*, Beryllium Corrosion Meeting Report, LANL (October 1997).
12. N. A. Lange (ed.), *Lange's Handbook of Chemistry*, revised 10th Edn. McGraw-Hill, New York (1967).
13. R. C. Weast (ed.), *Handbook of Chemistry and Physics*, revised 51st Edn. The Chemical Rubber Co., Cleveland, OH (1970).
14. D. M. Butler, *Cleaning Beryllium Parts, Building 444*, Rockwell International Confidential Document M-38539-1, Rocky Flats Plant, Golden, CO.
15. G. W. Bohnert and D. A. Carey, *Scale-Up of Recovery Process for Waste Solvents*, Technical Report KCP-613-4479, Kansas City Division, Allied-Signal Aerospace Company (February 1991).
16. J. Chastain and R. C. King, Jr. (eds), *Handbook of X-ray Photoelectron Spectroscopy*, Appendix B. Physical Electronics, Eden Prairie, MN (1995).
17. O. Kubaschewski, C. B. Alcock and P. J. Spencer, *Materials Thermo-Chemistry*, revised 6th edn. Pergamon Press, New York (1993).