THE ROLE OF ALKALINE CLEANING SOLUTIONS AND CL-CONTAINING LUBRICANTS ON PITTING CORROSION IN NiTi ALLOYS

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ABSTRACT

Alkaline cleaning agents are found to react with remnant manufacturing lubricants trapped in surface defects of a NiTi alloy to form Cl-based salts. These sub-surface "reservoirs" may act as nucleation sites for pitting corrosion either latent under ambient conditions, or on exposure to a limited range of high temperatures used to impart pseudo-elastic properties in these alloys as part of normal processing. The elevated temperature range over which corrosion was found to occur correlates well with published thermodynamic data for the liquid stability range of specific titanium chlorides. No corrosion is seen on exposure to higher temperatures. The combination of sufficient cavity size, amounts and ratios of reactive species viz., Cl and K (or Na), and water are thought to be necessary for a pit to evolve to a mature size.

KEYWORDS: CORROSION; PITTING; NiTi; TUBE; WIRE; LUBRICANT; CLEANING AGENT; DIE DRAWING

INTRODUCTION

The majority of corrosion studies performed on Nitinol (NiTi) are concerned with biocompatibility as regards formation of a stable, corrosion-resistant titanium i.e., nickel-free, oxide surface layer [1], or, dissolution of the base metal in-vivo situations which may lead to structural failure of an implant such as a stent [2]. Subsequent to fabrication into device geometry, implants are subjected to a variety of rigorous mechanical or chemical surface modification treatments such as tumbling, micro-blasting, and chemical or electro-polishing designed to reduce surface reactivity and improve biocompatibility and corrosion resistance. Quantitative analytical techniques such as potentiodynamic polarization testing are used to determine surface passivity of a manufactured implant, while more empirical techniques are used to study dissolution rates, typically by exposing a prepared sample to controlled environments simulating body physiology and monitoring resultant corrosion rates via material loss or surface degradation [3,4].

As a normal part of metal processing to final size metal surfaces are subject to combinations of heat, stresses associated with working operations, and a potential variety of lubricants necessary to reduce interfacial friction during die drawing of wire and tube products or rolling used in strip manufacture. Lubricants may be in powder or liquid form, either water- or petroleum-based; some of the most efficient solutions contain chemically active ingredients such as Cl or S which are known to be corrosive agents to Nitinol. These harsh environments adversely affect surface quality of the metal necessitating extensive surface cleaning subsequent to fabrication. While rigorous cleaning operations are performed on the processed metal to remove contamination, the effects of these aggressive manufacturing conditions on the corrosion resistance of Nitinol remain unclear. In light of infrequent corrosion pitting observed in manufactured Nitinol tubing, the present study was undertaken to examine the effects of two commonly used lubricants on pitting corrosion of a Nitinol alloy tube processed using typical conditions.

INITIAL OBSERVATIONS

Periodic examination of manufactured NiTi tubing and wire revealed infrequent pitting corrosion. Figure 1 shows a scanning electron microscope (SEM) image of a fully mature pit found either during inspection after 6-36 months storage under ambient conditions, tested in a 0.9% saline solution at 37°C, or subsequent to annealing at ~500°C. Pits varied in geometry from very round to misshapen with an average diameter of 50-100μm. A number of particulates are clearly visible within the pit shown in Figure 1. The associated energy-dispersive x-ray spectrum (EDS) of the particulates is also shown with a small + denoting the specific location at which the EDS spectra was obtained. As seen in the EDS spectrum a variety of elements were found within pits typically comprising C, Si, Cl, K, Na, S, Ca, Mg, P, and Al to one degree or another. Such examinations revealed no obvious source of pitting consistent with the fact that pitting appeared random. As such a series of investigations were initiated to determine the origins of corrosion pitting.

EXPERIMENTAL

Production-quality pit-free NiTi tubing of various dimensions from two manufacturers was chosen for corrosion testing and SEM/EDS analyses. Processing of tubing and wire requires application of lubricants with subsequent cleaning operations often using alkaline-based cleaning agents. Tubing samples that did not exhibit any evidence of corrosion pitting were submersed for 5 minutes in a 50% solution of a Cl-containing petroleum-based lubricant and an alkaline-based cleaning agent, commonly used in the manufacture of NiTi. A similar set of samples were submersed in another 50% solution containing a Cl-free water-based lubricant and the same alkaline-based cleaning agent used in the first solutions. Both sets of samples were superficially wiped off to remove excessive solution then heated in an air furnace for 10 minutes. One set of each samples were annealed at 530°C, a temperature in the range commonly used during final heat treating of Nitinol materials to impart pseudo-elastic properties. Another set of samples was annealed at 750°C, a temperature in the range typically used to fully anneal NiTi alloys. After annealing samples were submersed for 5 hours in a 0.9% saline solution maintained at 37°C to accelerate corrosion pitting then examined using light- and scanning electron-microscopy techniques. In all cases, secondary-electron imaging (SEI) conditions were used with a 20KeV accelerating voltage for obtaining SEM images.

RESULTS AND DISCUSSION

SEM AND EDS ANALYSES

Tubing samples from two manufacturers were subject to intensive SEM analyses over the course of a few days to aid in determining the source of corrosion pitting. Figure 2 shows the surface of a typical pit-free NiTi tube. Generally the surface is very clean and uniform. Associated EDS spectrum shows the primary constituents to be Ni, Ti, with a small amount of Al and O present, although Si is periodically also found. A uniform dispersion of small linear defects can also be seen over the tube surface in Figure 2. Typically, these linear defects have a large aspect ratio with a length of 100-300μm and width of ~1-5μm. Optical micrographs (not shown) of cross-sectioned samples show these linear defects are only a few microns deep. Figure 3 shows a high magnification SEM image of one such linear defect. Visible within the defect are a few particles with associated EDS spectrum clearly showing Al and O. The morphology and chemical composition of these particles indicate these as Al_2O_3. It is likely the Al (or Si) and O seen in the EDS of the general surface shown in Figure 3 are the result of alumina or silica particles, used as part of tube and wire cleaning processes, adhering to tube surfaces. These particles become embedded in tube surfaces during die drawing operations creating small depressions in the tube surface which then elongate during iterative drawing operations to form the large-aspect-ratio linear defects seen in Figures 2 and 3.

After ~20 cumulative hours exposure to the vacuum chamber samples began to exhibit an unusual phenomenon. Clearly seen on the left image of Figure 4 are the series of linear defects previously described albeit with a number of dark areas surrounding a few of the linear defects. The right image in Figure 4 shows a higher magnification view of the boxed area shown in the left image. The dark areas, termed "smears", are clearly visible. Examination of numerous samples showed that smears were consistently associated with linear defects. These smears tend to make the linear defects appear wider than shown in previous images. The EDS spectrum obtained on the smear is shown at the bottom of Figure 4 and is seen to contain an assortment of elements.

With increasing time of exposure in the vacuum chamber the smears increased in size. The left image in Figure 5 shows an example of a typical surface after ~336 cumulative hours in the vacuum chamber with the right image showing a higher magnification view of the boxed area. It is obvious that smears are significantly growing in size taking on a very liquid-like appearance. Additionally, a number of small white particles are seen in both images shown in Figure 5. Essentially consistent with the EDS analysis of the smaller smear shown in Figure 4 after 20 hours exposure to the vacuum, the EDS analysis of the smear shown in Figure 5 is seen to contain C, O, Si, Cl, K, Na, S, Ca, Mg, and Al, as well as, Ni and Ti. After sufficient time of exposure to the vacuum smears consistently exhibited a distinct liquid-like appearance with irregular, misshapen boundaries, appeared to emanate from linear defects, and contained essentially the same chemistry as a fully mature pit.

Figure 6 shows a particularly interesting smear in that it is round and contains a single distinct white cubic particle. Surrounding this smear are the linear defects previously described. The EDS spectrum of the round smear shown in this figure was consistent with those presented in Figures 4 and 5, while the EDS analysis of the white cubic particle, shown at the bottom of Figure 6, is seen to exhibit only K, Cl, and C, with a small amount of Al. Due to a large electron excitation volume a small amount of Ni and Ti are also seen. EDS analyses on other white particles consistently revealed these to consist of an alkaloid e.g., K, Na or Ca, and Cl. Based on these analyses it is reasonable to assume that the white cubic particle in Figure 6 is a KCl crystal apparently forming within the smear. It is also evident from this figure as well as analyses on numerous other samples, that smears are clearly associated with the linear defects.

Other than Al the elements consistently found in the smears comprise the chemical formulation of either drawing lubricants or alkaline-based cleaning agents both of which are used during the normal course of Nitinol tubing and wire manufacture. It is thought that these fluids become trapped within the linear defects during processing. While tube and wire cleaning processes are generally sufficient to remove these lubricants, periodically some of these fluids remain trapped within the linear defects. It is speculated that extended exposure to the relatively high vacuum environment in the SEM specimen chamber allowed these fluids to percolate from within these "sub-surface reservoirs".

While previously described observations and analyses of smears and fully mature pits are indicative of a corrosion process, it would be beneficial to analyze a corrosion pit in its incipient stage. Figure 7 shows what is thought to be one such corrosion pit. This pit exhibits several important characteristics. In contrast to a fully mature pit it is ~7µm in diameter i.e., about one-tenth the size of a fully mature pit. Visible within this pit are two particles the EDS analyses (not shown) of which revealed them to be an Al_2O_3 particle and KCl crystal consistent with analyses on particles found in linear defects and smears, respectively. Although somewhat difficult to see in Figure 7, this small pit is clearly forming within a linear defect.

Perhaps most important however in Figure 7 is the fact that the lower edge of the corrosion pit exhibits a distinctly brighter contrast than the surrounding pit-free NiTi surface. In fact, the brighter image of the lower pit edge is more consistent with the contrast of the white particles seen in Figures 5 and 6. EDS analysis of the lower edge of this pit is shown at the bottom of Figure 7. This spectrum clearly shows the edge of the pit contains a substantial amount of both K and Cl. Subjecting this pit to various imaging conditions to include using back-scattered electrons rather than secondary electrons eliminated the possibility of the brighter contrast seen on the lower edge of this pit being the result of edge effects common in SEI analyses. Although the features of the lower edge of the incipient pit shown in Figure 7 are consistent with those of the white particles, there is a profound difference in morphology between the two. Rather than existing as a distinct KCl crystal, the K + Cl is coated over the lower edge of the pit conforming to its shape. This is important in that it is speculated that this represents an actual corrosion front emanating from a linear defect outwards into the NiTi bulk metal. This observation provides further evidence for proposing a pitting corrosion mechanism that may occur in NiTi tubing and wires as discussed in the following section.

LATENT-PITTING CORROSION

Based on the above observations it is speculated that linear defects are induced by Al_2O_3 or SiO_2 particles adhering to, and becoming embedded in, tube surfaces during drawing operations thus creating a series of small surface depressions. Further drawing operations result in elongation of the surface depressions to form linear defects. These defects act as sub-surface reservoirs trapping petroleum-based Cl-containing lubricants that are commonly used in

the manufacture of Nitinol tubing and wire. Subsequent surface cleaning operations that use alkaline-based cleaning agents in liquid form may also become trapped in these sub-surface reservoirs thus providing the potential morphological and chemical conditions conducive to corrosion pitting.

It is thought that latent corrosion pitting is occurring under long term storage conditions as a result of an alkaloid from the cleaning solution reacting with Cl in drawing lubricants, to form a simple salt compound such as KCl, NaCl, or CaCl within the linear defects. The halide salt compounds are relatively stable in dry environments, however exposure to slightly elevated temperatures and high-humidity conditions encountered, for example, either during ETO sterilization cycling or long-term storage in specific geographic locations, may result in salts hydrolyzing to form HCl. TiO_2 is highly chemically resistant and is attacked by very few substances however Ti alloys are known to be subject to localized attack in tight crevices which are exposed to Cl, Br, I, F, or S-containing solutions [5]. Because of the small, restricted volumes of solution in these crevices, crevice pH levels as low as 1 or below can develop. These local reducing acidic conditions can result in severe localized active corrosion within crevices resulting in the pitting observed under ambient conditions over extended periods of time.

While the observations, results and analyses presented thus far provide an explanation for latent pitting occurring under what are essentially ambient conditions, they do not provide an explanation for corrosion pitting found directly after thermal aging treatments. The following section describes the results from the controlled annealing experiments in order to determine the role of high temperatures on corrosion pitting in these alloys.

ELEVATED-TEMPERERATURE EFFECTS

Figure 8 shows an SEM image of a sample that was immersed in the 50% solution of the Cl-containing lubricant and alkaline cleaning agent and annealed at 530°C for 10 minutes. Clearly seen in this figure are a number of small and large corrosion pits. Associated EDS analysis obtained within one of these pits is shown at the bottom of Figure 8. Consistent with analyses of corrosion pits formed under ambient conditions, this pit is found to contain C, O, Na, Al, S, and Cl, with a small amount of Si present. Figure 9 shows an image of a sample that was immersed in the Cl-containing lubricant/alkaline cleaning agent solution and annealed for 10 minutes at 750°C. There was no evidence of corrosion pitting on this sample. Similarly, no evidence of corrosion pitting was observed on samples that were immersed in the Cl-free lubricant/alkaline cleaning agent solution and annealed at 530°C and 750°C.

These experimental findings are consistent with observations made during manufacturing. Over the course of normal inspection of as-manufactured product surfaces, it was noted that on those infrequent occasions when corrosion pitting was found it was consistently after final annealing operations. No evidence of pitting corrosion was ever found directly after the higher temperature anneals. Review of published thermodynamic data [6] for the liquid stability range of titanium chlorides shows Ti_3Cl to be stable as a liquid in the temperature range of 440°C < T < 660°C. It is also over this temperature range that TiO_2 is known to reduce in the presence of Cl and C to form Ti-chlorides, as is used in the Kroll process during production of Ti sponge [7]. These temperatures correlate well with those typically used for final annealing of Nitinol alloys typically 450°C < T < 550°C. It is thought that TiO_2 thus reduces to form liquid Ti_3Cl in this range of temperatures, which then corrodes the base metal. Exposure to the higher temperatures used during in-process full anneals viz., 600°C < T < 800°C results either in volatilization of trapped lubricants or formation of an oxide layer sufficiently thick to resist corrosion of the base metal.

Slight modifications to the manufacturing process easily eliminated observations of pitting corrosion. The modifications include implementation of more robust cleaning and rinsing processes, replacing the Cl-containing petroleum-based lubricant with a water-based Cl-free lubricant, and utilizing alternative surface treatments to sand blasting to prevent linear defects from forming.

SUMMARY

The discussions presented herein provide the basis for describing a mechanism by which pitting corrosion was infrequently found to occur in production-quality Nitinol tubing and wires either latent after 6-36 months storage under ambient conditions, after testing in a 0.9% saline solution at 37°C, or subsequent to final annealing at ~500°C. It is proposed that a series of shallow linear defects form during tube and wire drawing operations as a result of either Al_2O_3 or SiO_2 particles used in sandblasting operations. These particles adhere to and become embedded in the NiTi surface. As these linear defects form on the surface, lubricant becomes trapped within these small sub-

surface reservoirs. Subsequent surface cleaning operations using alkaline-based cleaning agents in liquid form may also become trapped in these sub-surface reservoirs. Further rinsing operations remove virtually all remnant-manufacturing fluids. Infrequently, however, some of these fluids remain within the linear defects thus providing the potential morphological and chemical conditions conducive to crevice corrosion. It is speculated that latent crevice corrosion may occur in these alloys as a result of an alkaloid from the cleaning solution reacting with Cl from drawing lubricants to form a simple salt compound such as KCl, NaCl, or CaCl. Temperature-humidity conditions encountered during ETO sterilization cycling or during long-term storage in specific geographic locations can result in decomposition of salts to form HCl which then corrodes the NiTi metal surfaces.

Repeatable corrosion pitting occurred on pit-free samples that had been coated with a solution of the Cl-containing lubricant and alkaline cleaning agent and heated to 530°C, a temperature in the range of those typically used to impart pseudo-elastic properties in NiTi alloys. No pitting was observed under similar conditions at 750°C used to fully anneal these alloys. At the lower thermal aging temperatures TiO_2 reduces to form liquid Ti_3Cl which corrodes the base metal, whereas exposure to the higher temperatures results either in volatilization of trapped lubricants or formation of an oxide layer sufficiently thick to resist corrosion of the base metal.

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Revised Figures for manuscript #4:

Original Manuscript	Revised Manuscript
Figure 1	Figure 1
Figure 2	Delete
Figure 3	Figure 2
Figure 4	Figure 3
Figure 5	Delete
Figure 6	Figure 4
Figure 7	Figure 5
Figure 8	Figure 6
Figure 9	Figure 7
Figure 10	Figure 8
Figure 11	Figure 9
Figure 12 and 13	Delete

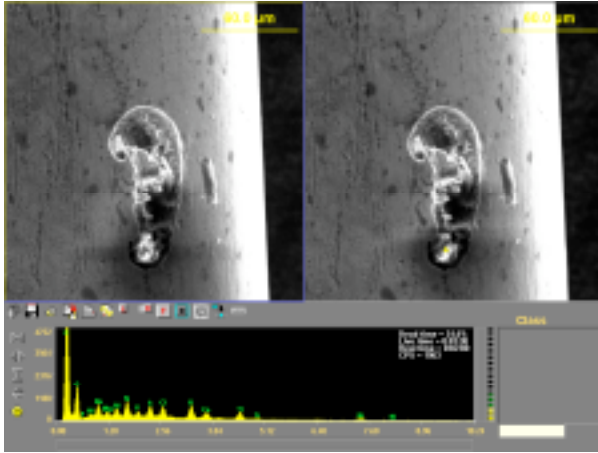**SEE NEXT PAGES FOR FIGURES 1-9.**

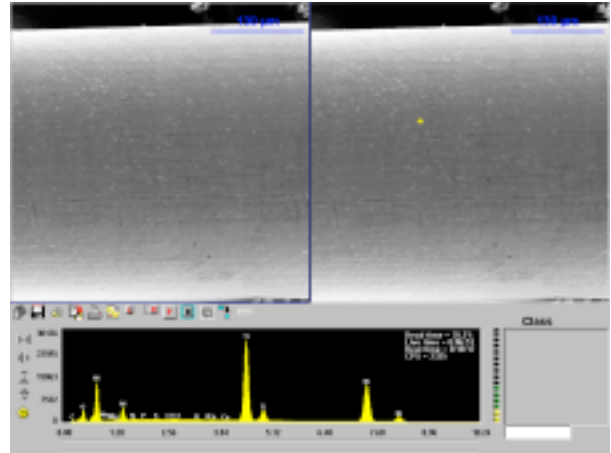*Figure 1. Typical corrosion pit.*

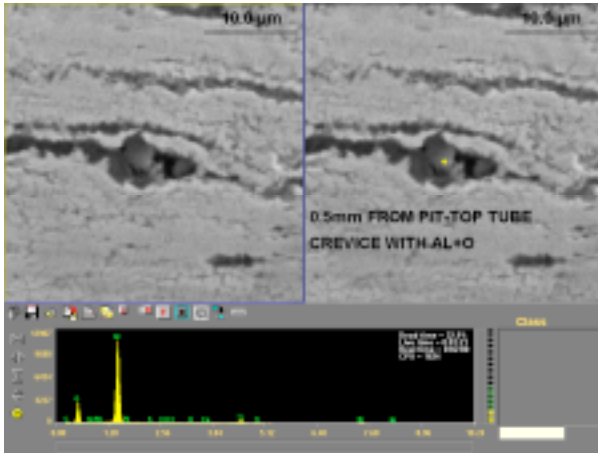

Figure 2. Typical pit-free tube surface.

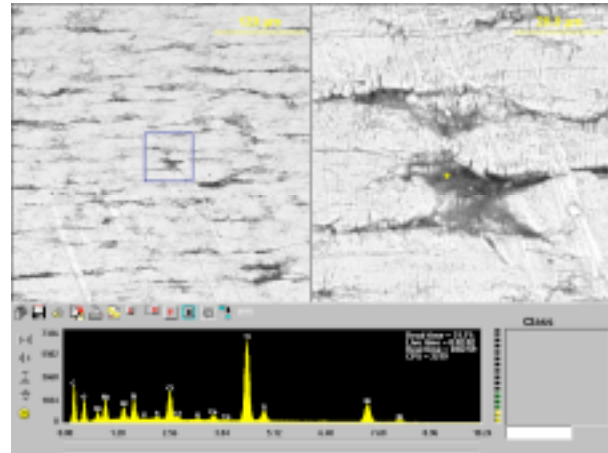*Figure 3. Typical linear defect.*

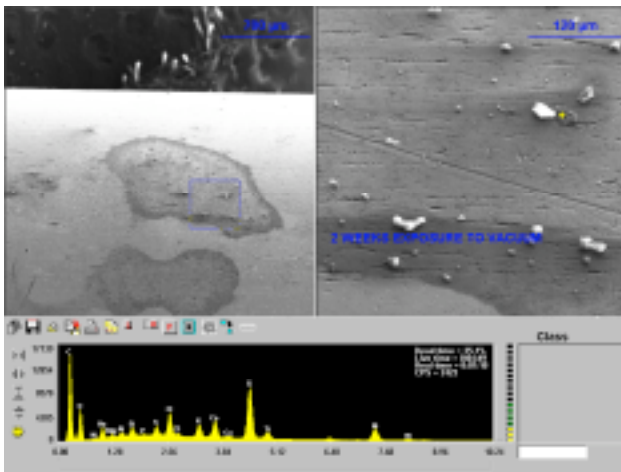*Figure 4. "Smear" after 20 hours of SEM testing*

Figure 5.'Smears" after ~336 cumulative hours in the vacuum chamber.
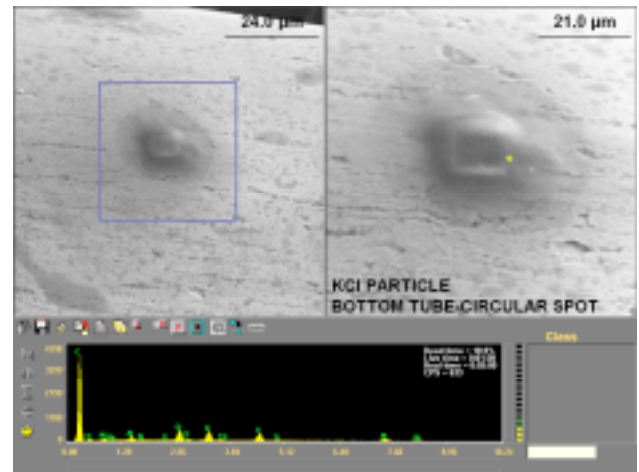

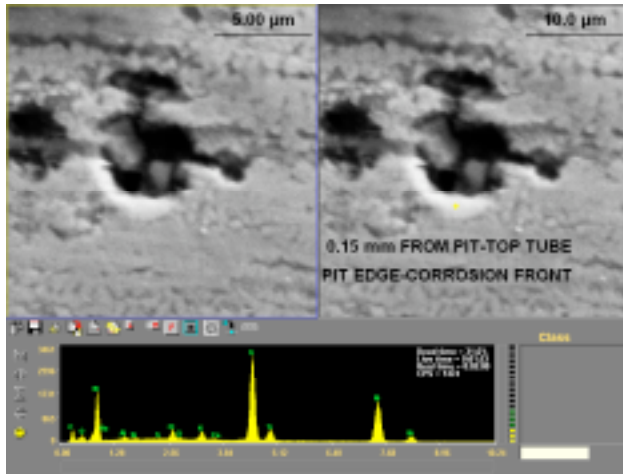
Figure 6. Round "smear" containing KCl crystal.
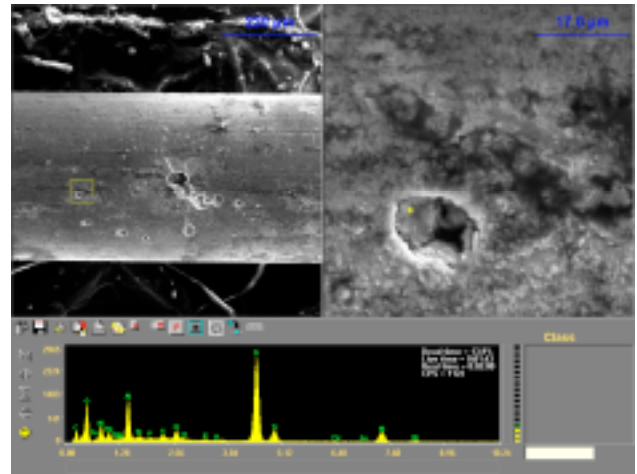
Figure 7. Incipient corrosion pit.

Figure 8. Sample immersed in Cl-containing solutionHeat treated at 530°C.
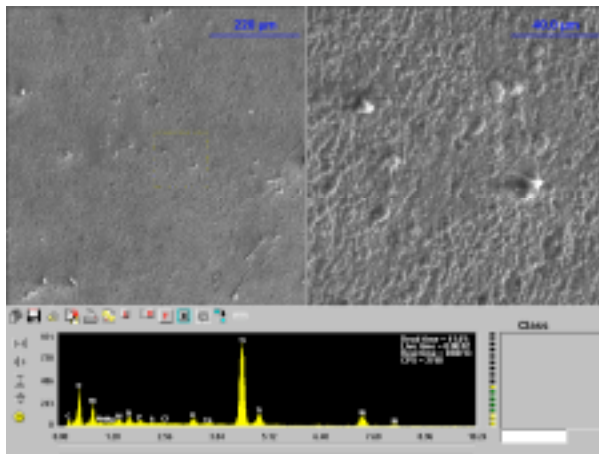

Figure 9. Sample immersed in Cl-containing solution. Heat treated at 750°C.