Comparison of the Chromium Distribution in New Super Koropon Primer to 30 Year Old Super Koropon Using Focused Ion Beam/Scanning Electron Microscopy

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Introduction

Super Koropon primer (MB0125-055) plays a significant role in the corrosion protection of areas throughout the Orbiter. Because the Orbiter Program relies so heavily upon the performance of the Koropon primer, it is necessary to fully understand all aspects of the behavior of the coating.

One area where little understanding of the Koropon primer still exists is the level of risk associated with age related degradation. Recently, efforts were undertaken to better understand the age life of the Koropon primer and to gain some insight into the aging process of this coating. In that study, an aluminum access panel from the Orbiter Enterprise was used to investigate the performance of the old Koropon film. A control panel was also used to study the performance of new Koropon coating. Preliminary investigations into the performance of aged Super Koropon primer, MB0125-055, indicated a significant decrease in corrosion protection. After only 500 hours of salt fog testing (ASTM B117), corrosion was observed in the scribe line of the access panel from the Orbiter Enterprise. Corrosion was also observed away from the scribe after 1000 hours of salt fog testing, while the freshly applied Koropon coating easily passed the 1500 hour salt fog test with no corrosion. As a result, subsequent testing was performed to determine the cause of the corrosion on the panel from the Orbiter Enterprise after salt fog testing. The results obtained indicated that the Enterprise Koropon may have reduced levels of chromate in the film and/or the chromate may be poorly distributed within the thickness of the film.

Further analysis of both the Enterprise Koropon and the freshly applied Koropon was performed to determine the distribution of chromium within the matrix of the film.

Procedure

The control Koropon sample and the Enterprise Koropon sample were mounted on scanning electron microscopy (SEM) sample studs using silver paint. In an effort to minimize the possibility of charging during SEM analysis, both samples were further sputter coated with a gold/palladium film. A Quanta 3D Dual Beam focused ion beam/scanning electron microscope (FIB/SEM) was used to mill a cross section of the Koropon sample from the Enterprise sample and the freshly applied Koropon sample, obtain FIB and SEM images, and SEM-XEDS data.

Results and Discussion

The SEM images of the surface of the Koropon sample from the Orbiter Enterprise and the control Koropon sample are shown in Figures 1(A) and 1(B), respectively. Even though the SEM image of the surface of the Enterprise sample is at a slightly higher magnification, the differences in the two surfaces are readily apparent. The surface of the Enterprise sample is very rough and “flakey” while the surface of the control sample appears to be much smoother. The chromium is very visible on both surfaces. The chromium appears as light “dots” on the surface of both samples. A higher magnification

FIB image of the surface of the control Koropon sample is shown in Figure 2(A). The smooth surface can be seen in much greater detail in this image. A region containing chromium is also labeled in the image and the SEM/XEDS spectrum obtained from this region is shown in Figure 2(B). The platinum in the spectrum may be attributed to the platinum that was deposited on the surface to protect the region of interest from damage during the milling process. The gallium may be attributed to the gallium ion beam used to image in FIB mode and also used to mill the SEM trench cut. The titanium and oxygen in the spectrum may be attributed to the paint used to mount the sample. The sulfur, silicon, magnesium, and carbon may be attributed to the epoxy resin of the Koropon matrix.

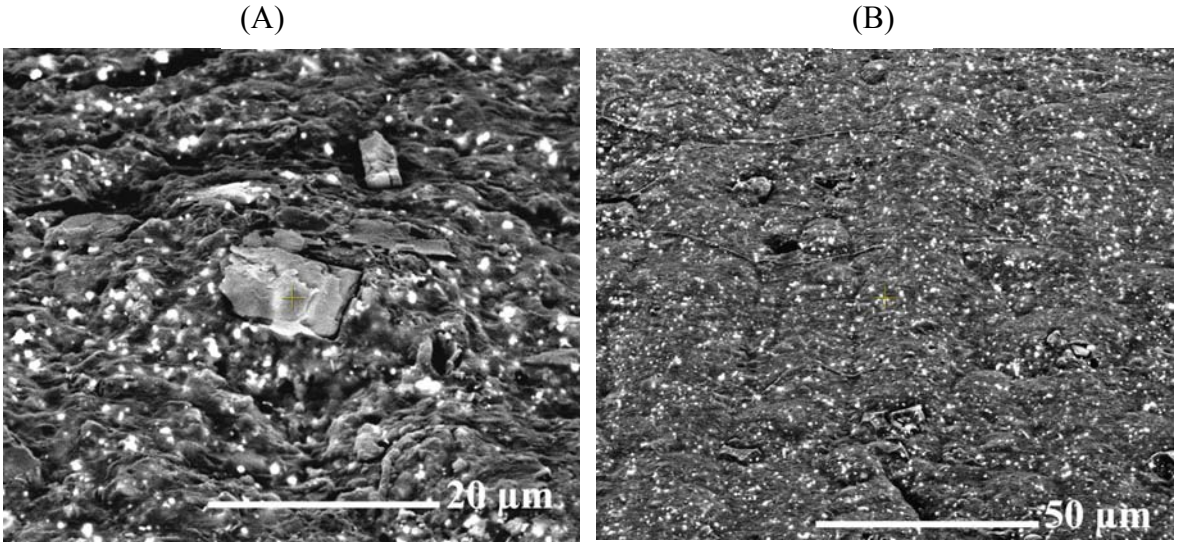
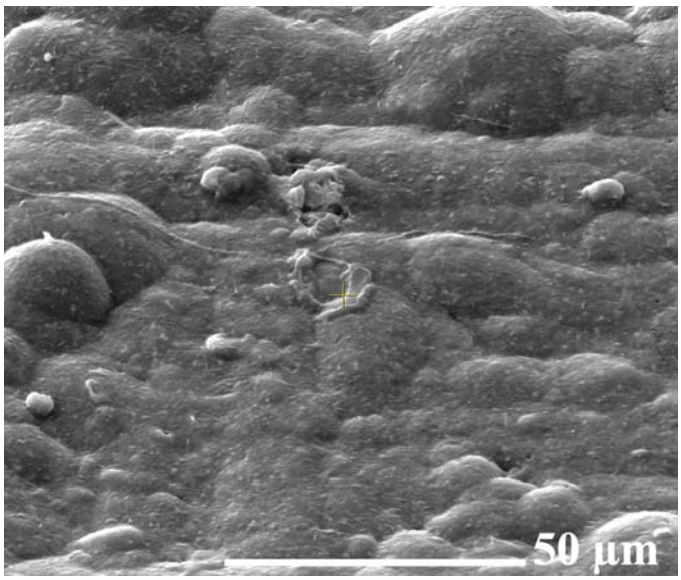


Figure 1. (A) BSE-SEM image of the surface of the Koropon sample from the Orbiter Enterprise. (B) BSE-SEM image of the surface of the Koropon from the control sample.

(A)



(B)

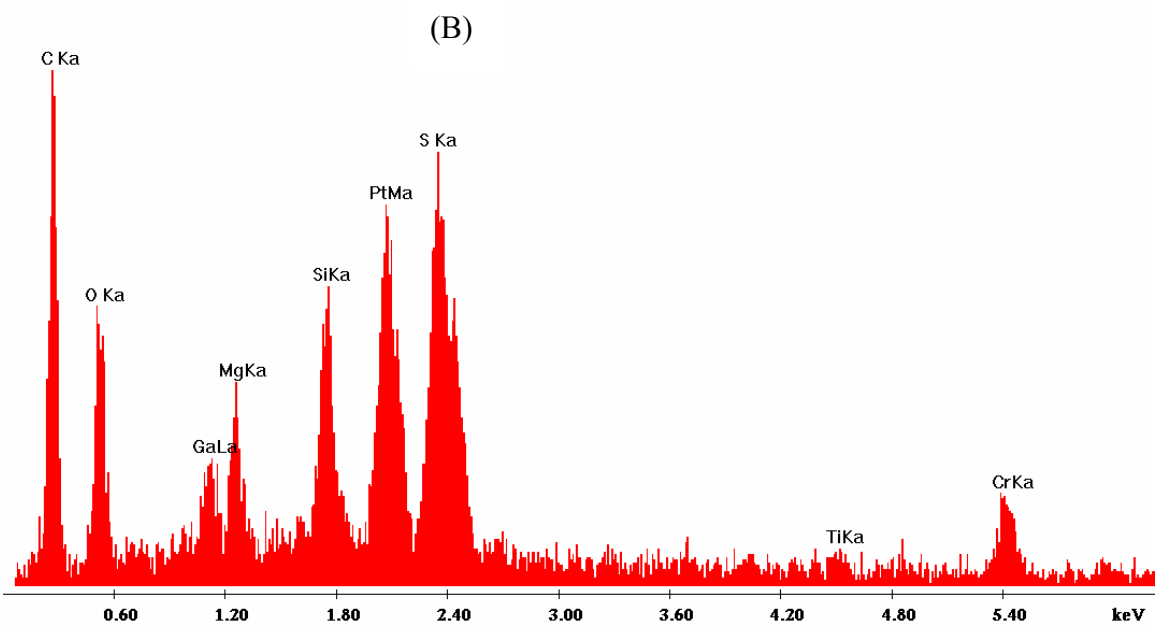


Figure 2. (A**)** FIB image of a region of the surface on the control Koropon sample. (B) SEM/XEDS of the chromium region of the surface of the control Koropon sample shown in (A).

The cross-section BSE-SEM images for the Enterprise Koropon and the control Koropon films are shown in Figure 3(A) and 3(B), respectively. The platinum pad that was deposited to protect the surface of the region of interest from the gallium ion beam during milling is labeled in both images. There was also a void (labeled Pt in the bulk matrix)

that filled with redeposited platinum during milling. Again, the chromium appears as light "dots" and/or very light regions in both images. There are some regions of chromium just beneath the surface that appears as light gray areas. The overall particle size distribution varies widely, however some of the chromium particles were larger than expected. This may be due to some particle agglomeration.

The SEM image of the Enterprise Koropon sample shows that there is a significantly reduced level of chromium in the coating in this region as compared to the new Koropon film. A region 25 µm × 8 µm × 5 µm was milled (each slice was 162 nm thick) to determine the distribution of chromium over a selected area. SEM images were obtained after each slice. These SEM images show that the chromium appears to be poorly distributed within the film. In fact, there were areas of the old Koropon film that had even less chromium than was observed in Figure 3(A), while other areas had higher chromium content.

The control sample appeared to have a considerably increased quantity of chromium as compared to the Enterprise sample. The chromium in the control film also appeared to be more evenly distributed. Examples of the SEM-XEDS data obtained from the chromium regions of both samples are shown in Figure 4(A) and 4(B). The chromium Kα energy for both Koropon samples can be observed at 5.414 keV in the spectra. Because the electron beam is large and the chromium regions are small, XEDS data from the surrounding matrix and platinum layer can be observed in the spectra.

(A) (B)

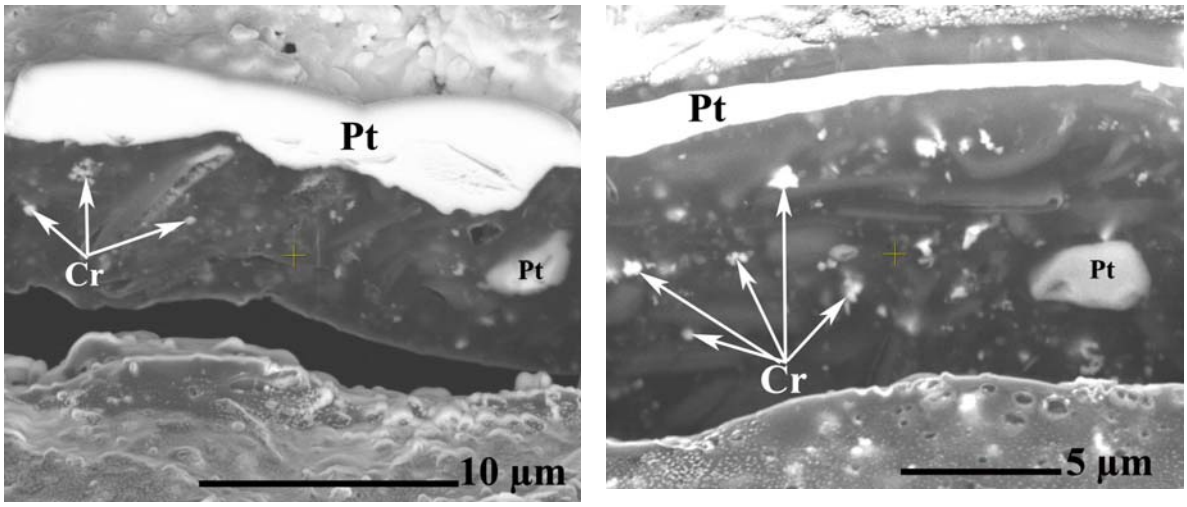
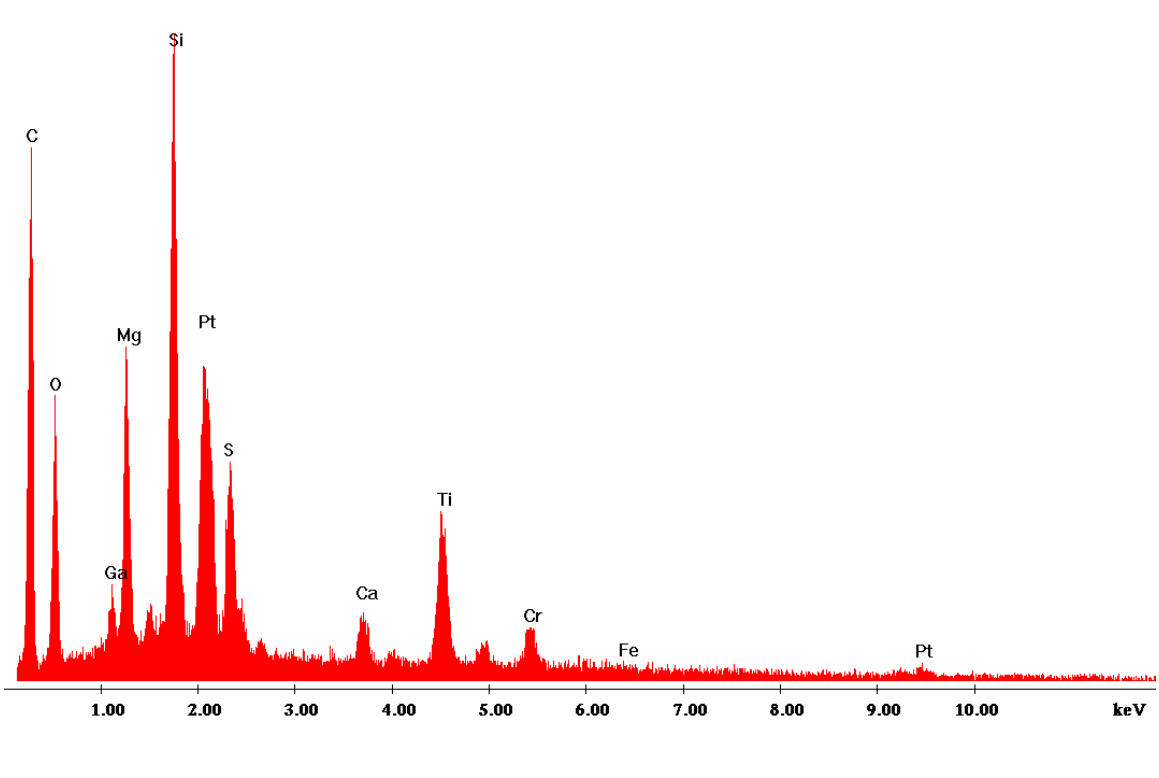


Figure 3. (A) BSE-SEM image of the Enterprise Koropon sample showing the chromium distribution throughout the matrix in this region. (B) BSE-SEM image of the control Koropon sample showing the chromium distribution throughout the matrix in this region.

(A)



(B)

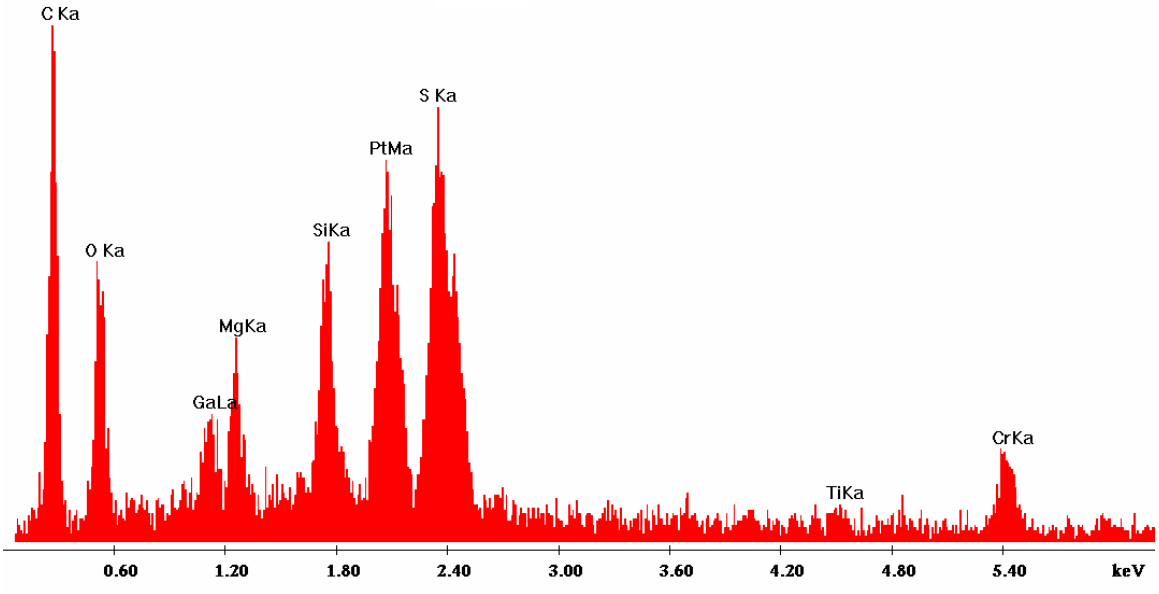


Figure 4. (A) SEM/XEDS Spectrum of the region denoted by the middle arrow in Figure 3(A). (B) SEM/XEDS Spectrum of the region denoted by the second arrow from the right in Figure 3(B).

Another interesting observation was the differnce in coating thickness. The Enterprise Koropon film, Figure 5(A), was approximately 8 µm (0.000315 inches) thick where as the control Koropon coating, Figure 5(B), was more than 10.5 µm (0.000413 inches) thick. Note that the sample was not cut all the way through. This measurement suggests that the old Koropon film was much too thin since the specified Koropon thickness is 0.(0006 to 0.0009 inches). One possible explanation for this discrepancy is degradation of the polymer matrix of the Enterprise Koropon film as a result of aging and/or as a result of interaction with the stripper used to remove the coating from the panel. This is very plausible since the physical appearance of the Enterprise Koropon sample and the control Koropon sample differed. The old Koropon film was slightly darker in color and appeared to be more brittle than the control Koropon film.

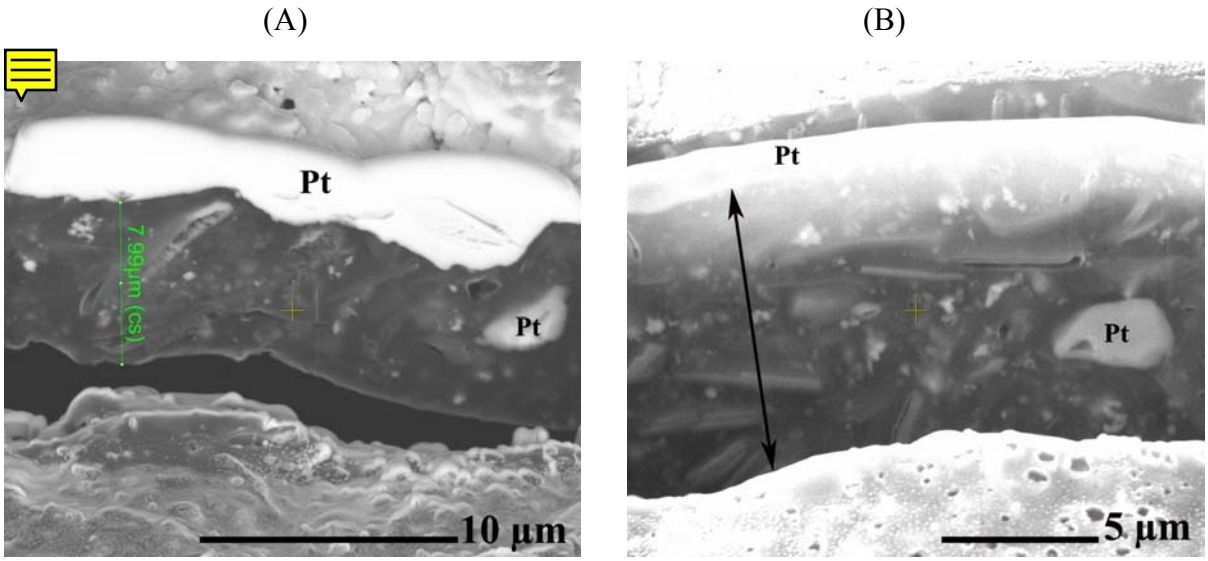


Figure 5. (A) BSE SEM image of the cross-section of the Enterprise Koropon sample used for the measurement of the thickness of the film. (B) SEM image of the cross-section of the control Koropon sample used for measurement of film thickness. (Note that the measurement bar would not save on this image. The location of the thickness measurement is denoted by the arrow).

Conclusions

The poor performance of the 30 year old Koropon in a corrosive environment appears to be directly related not only to a reduced level of chromium, but also to the uneven distribution of the chromium within the matrix of the film. In some regions of the film, the chromium level was very little while in other areas an increased chromium level was observed. When comparing the Enterprise Koropon film to the freshly applied film, it appeared that the old Koropon film had a reduced level of chromium overall. There appeared to be a higher level of chromium in the control Koropon film that was more evenly distributed.

The inconsistency in the thickness of the coating of the Enterprise Koropon and the specified Koropon thickness may be due to degradation of the polymer as a result of aging and/or the degradation as a result of chemical interaction between the polymer and stripper used to remove the coating from the access panel.

Further investigations should be performed to better elucidate the corrosion resistance of the Koropon primer over time.