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MODERN MICROSCOPY - On the Light Side!

MICROANALYSIS SURPRISES

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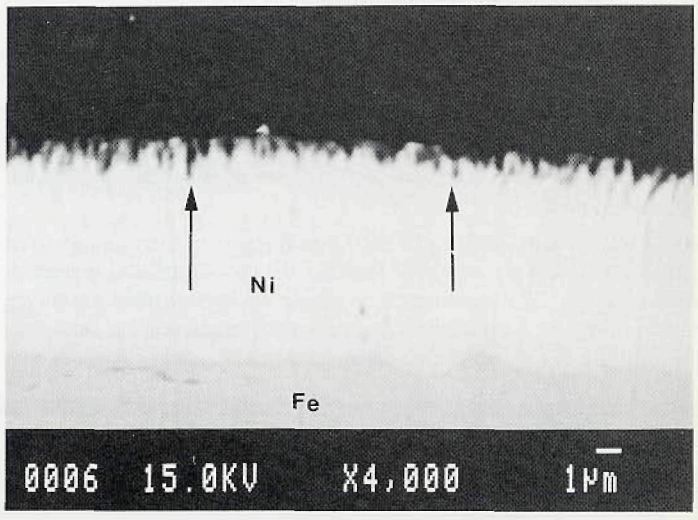
How many of the analytical chemists reading this will identify with the following scenario? A customer gives you a sample with a contaminant and asks you to identify the material. Your customer provides a very logical dissertation on what the material is likely to be. With that bias firmly entrenched in your mind, you proceed with the analysis, fully expecting to find what your customer said you should. However, during the course of your analysis, you discover that the contaminant is something completely different than expected. Now you are presented with the dilemma of facing that customer to explain the "unexpected" result. You are immediately put on the defensive by being accused of not having properly calibrated instruments or you have obviously contaminated the sample with something else during sample preparation, etc. These situations occur in laboratories all over the world.

At McCrone Associates, we specialize in microanalysis (e.g. small particles, thin films and surface chemistry). Our clientele are from all walks of industrial life and the types of samples that we receive are usually not routine analysis problems. Therefore, we get more than our share of analysis surprises. I am going to share some of my "war stories" with you because there are valuable lessons to be learned from these experiences.

NICKEL "OXIDATION"?

A nickel plated steel rod was submitted to identify a dark gray/black blotched stain on the surface of part of the rod. The client was reasonably certain that the stain was from oxidation of the nickel plating. Samples from the stained and non-stained areas were mounted for analysis in the electron microprobe which is equipped with an energy-dispersive x-ray (EDX) analysis system with light element detection capability. Naturally, I was looking for differences in oxygen content in the stained versus non-stained areas, fully expecting to to see higher oxygen in the stain. However, I found that the oxygen signal was quite low and nearly equal for both surfaces. With the oxygen bias firmly entrenched in my mind, I proceeded to do a relatively thorough troubleshooting of the EDX system to ensure that it was, in fact, properly detecting oxygen. When I was satisfied that everything was in good working condition, I pondered over alternative analysis.

I tried scraping the surface with various microtools, but only succeeded in scratching it and not removing anything. Further analysis by reflectance infrared microspectroscopy revealed that there was no detectable organic material. In absolute desperation, I decided to do a metallographic examination on a cross section of the sample. The SEM micrograph shown here reveals the cause of the dark stain. The surface of the nickel is etched into a "sawtooth" pattern, only about 1-2 μm deep. The dark stain was merely an optical effect caused by refraction and absorption of light within the pits.



SEM micrograph of the nickel plated steel rod cross section showing the "sawtooth" etch pattern (arrows) in the nickel plating

HIGH RESISTANCE ELECTRICAL CONTACTS

Several samples of electronic switches were submitted to determine if contamination was the cause of high resistance readings on some of the electrical contacts.

During examination with a light microscope, I found no evidence of visible contamination. Further analysis by energy-dispersive x-ray spectrometry revealed no inorganic materials other than the gold plating. Infrared microspectroscopy using the reflectance mode also revealed no evidence of organic material. (Does this sound familiar?)

When I called the client with my results, he insisted that there has to be a contamination on the surface to cause such high resistance readings. So I agreed to continue the analysis, wondering in the back of my mind what I was going to do next. I decided to examine the contact surfaces using backscatter electron imaging. Using this technique, elements with higher atomic number appear as whiter regions. In this case, gold, being a very high atomic number element, would show up very bright. After manipulating the microscope operating parameters, small blotches of darker gray material (lower atomic number) became visible on the surface of the gold. The morphology of the blotches indicated a very thin organic film.

After taking some low magnification micrographs to use as "maps" I re-examined the samples in the infrared microspectroscopy system. Using the SEM maps, I was able to locate the areas where the blotches occurred even though I could not see them optically. Because the films were quite thin, the infrared spectra required some software manipulation in order to improve the signal-to-noise ratio. However, a spectrum was obtained and revealed the presence of a bisphenol-A epoxy. The client, upon hearing the results, was able to eventually track down the source of the problem and duplicate in their

laboratory. In this case, thanks to the persistence of the client, we were able to help solve their problem.

CONVERSION COATING ON ALUMINUM BEVERAGE CAN ENDS

I was preparing a presentation for InterMicro '93. As part of the presentation, I was going to show the differences in quantitative analyses of a chromate/phosphate conversion coating. Measuring the percentages of chrome and phosphorus in these types of coatings can be deceiving because they are such thin films. In the electron microprobe, the accelerating voltage determines the depth of the analysis envelope. Therefore, if you start out with high accelerating voltage, you obtain an EDX quantitative analysis which shows lower chrome and phosphorus compared to using lower accelerating voltages. In addition to comparing EDX quantitative analysis, I was also going to include quantitative analysis using ESCA. With ESCA surface analysis, the depth of penetration for the analysis is only tens of angstroms rather than micrometers.

I gave one of my colleagues a sample of an aluminum beverage end and asked him to perform the ESCA quantitative analysis for chrome and phosphorus for my presentation. The data revealed a significant amount of zirconium on the surface. From my previous experience (working in the can industry for many years), I was not aware of zirconium as a component of the chromate/phosphate conversion coating on aluminum ends (which is applied at the aluminum mills).

Now I found myself in a reverse role where I am the customer. I asked my colleague to double-check that result and do another scan because I felt that zirconium should not be present. He reported that he had done a couple more scans and found the same result. There was a significant amount of zirconium on that sample! Once again, the mind set was beginning to entrench deeper. I obtained another can and asked my colleague to conduct ESCA analysis of the end. After the analysis, he informed me that there was a significant amount of zirconium on this sample also. At that point, I had no choice but to believe that data and I went ahead and included it in my presentation. I am still mystified by that result and I will contact some of my friends in the aluminum industry to get an explanation. This is a good example of how reliance on one technique may not provide a complete answer.

DISCUSSION

I mentioned earlier that there are lessons to be learned from these experiences. As analysts, we are all responsible for answering the basic question, "what is this stuff?" And, as we all know, providing the right answer is not always easy and requires persistence by not only the analyst, but also the customer. It is very important to maintain good communications to get as much background information about the samples as possible. Most of the time, that background information is critical and extremely helpful for the analysis but, as I have shown here, sometimes the background information may be misleading. All too often, the analyst is constrained by time factors where the customer needs results immediately and you do not have the luxury of time to thoroughly analyze the samples. As an independent laboratory, charging analysis time by hourly rates, budget constraints form the customer's side often limit the thoroughness of our analysis. The risk with any of these constraints, naturally, is that a partial analysis may not provide the correct answer and decisions made on the basis of that analysis may also be wrong. If, however, you do not have these constraints, let your natural curiosity take over. You can even go so far as to doubt your own data and try other techniques to verify the results. You never know, you may stumble into one of those "surprises" that will solve the problem Remember, things are not always what they seem to be. ■

*This newsletter is, of course, not nearly as "interesting" as it could be. To make it worthwhile, for you to read and for us to publish, we need **your** assistance in providing articles and material. We would particularly appreciate articles relating to advances in, and approaches to, the broad technology.* - - - *Editor*