

Microscopic Investigations of Sulfur - Rich Corrosion Products on Copper

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Formation of localized deposits was discovered on a conductive copper tape (Figure 1) while conducting scanning electron microscopy (SEM) examinations of high strength low alloy steel (HSLA) corrosion samples. The conductive tape was used ground the sample. The corrosion samples were tested in deaerated 5% NaCl solution buffered with $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ at pH=12 and $\text{CO}_2/\text{NaHCO}_3$ at pH=7, both at 20°C. Both solutions were in contact with H_2S . The partial pressure of H_2S ($p_{\text{H}_2\text{S}}$) was the same in each solution and was equivalent to 0.83 kPa [1].

SEM examinations of these localized deposits revealed their crystalline structure as shown in Figure 2 as an example. Also this deposit was used for determining elemental chemical composition at a selected site by energy dispersive x-ray spectroscopy (EDS) as a function of accelerating voltage. This site is also indicated in Figure 2

The EDS analysis found the composition in this site s to be primarily copper, sulfur, and traces oxygen. Figure 3 shows the chemical composition for copper and sulfur determined at 4, 5, 6, 7, 8, 9, and 10 kV. The S concentration decreases with increasing the voltage whereas the Cu concentration decreases with increasing the accelerating voltage. An important part of the EDS is to recognize that the local deposit size is comparable with the volume of the sample excited by the electron beam that produces X-rays for analysis. Quantification of Cu and S spectra and calculations of Cu:S atomic ratios found them to be close to Cu_2S . Although several stable copper-sulfur-based precipitates exist, Cu_2S has the lowest solubility product constant value of 10^{-48} among them [2]. Literature data [3] indicate that traces of sulfur compounds present in air can tarnish copper surfaces. The tarnish film can contain Cu_2S along with CuS and Cu_2O compounds

However, the copper tape was stored with the corrosion samples in a desiccator to keep them under a controlled atmosphere. . The corrosion samples were examined initially with the corrosion layer intact. Sulfur content varies depending on test parameters used. The Cu_2S crystals were observed on copper tape that had only four days in the desiccator with one coupon. It is highly possible that a trace of FeS-rich film present oh the corrosion samples underwent hydrolysis generating $\text{Fe}(\text{OH})_2$ and hydrogen sulfide. The former was scavenged by the copper tape. This resulted in the formation of Cu_2S that has the lowest solubility product constant [2].

References

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- [3]. H.H. Uhlig, R.W. Revie, Corrosion and Corrosion Control, 3rd edition, John Wiley & Sons, 1985, p. 171.

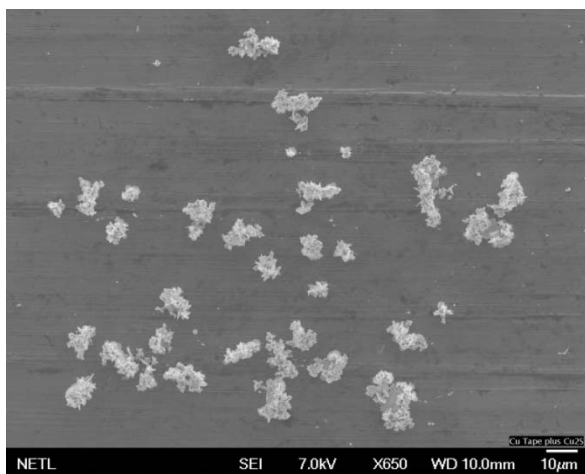
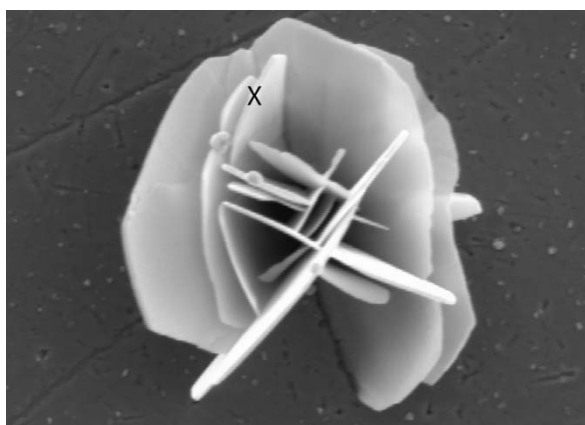


Figure 1: Formation of localized deposits on conductive copper tape.



3 µm

Figure 2: SEM secondary micrograph of Cu_2S -rich crystalline deposit used for EDS analysis. X-is site selected for EDS analysis.

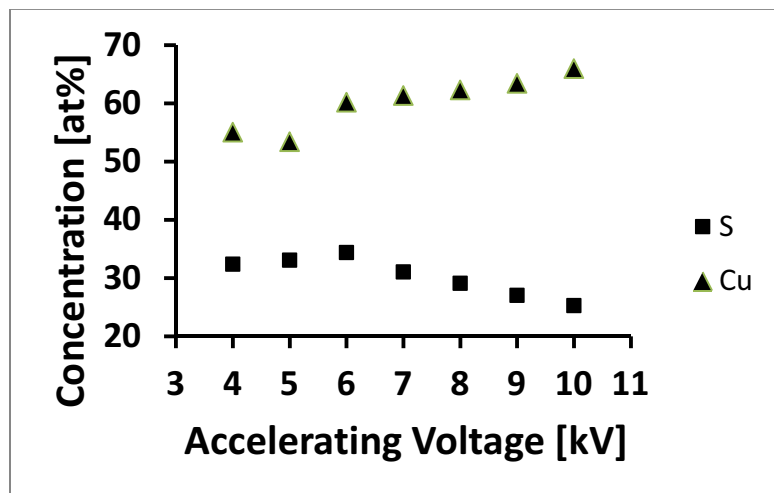


Figure 3: Concentrations of copper and sulfur determined by EDS as a function of accelerating voltage.