

pH Microsensors Allow Local Measurements of Pitting Corrosion at MnS Sites in Stainless Steel

MnS inclusions in stainless steel provide initiation sites for pitting corrosion. Jung O. Park and Hans Böhni from the Institute of Materials Chemistry and Corrosion in the Swiss Federal Institute of Technology used pH microsensors and microelectrochemical cells to observe the transient pH fluctuations as well as electrical activities during the dissolution of MnS inclusions in chloride and nonchloride solutions. There is a marked deviation in both transient pH and electrical current density from the norm during the commencement of MnS inclusion dissolution as reported in the September issue of *Electrochemical and Solid-State Letters*.

AISI 304 stainless steel samples with well-isolated MnS inclusions were placed in 1M Na₂SO₄ (pH 5.6) and 0.1M NaCl (pH 5.4) solutions. A pH microsensor, 10 μm in diameter, was embedded in a capillary, 100 μm in diameter. The microsensor tip was held 50 μm away from the sample surface. The electrochemical cell was comprised of a Pt counter electrode and a standard calomel electrode. Potential sweeps from -300 mV and up were performed at a rate of 0.2 mV/s for the nonchloride solution and 0.5 mV/s for the chlorinated solution. The researchers have found that for the nonchlorinated sample, an increase in current activity was detected at 300 mV, and at the same time, its pH fell to a minimum of 4.1 before returning to the proper value. For the chlorinated solution, current activity increased between 380 and 520 mV, while the pH dropped to 2.4 at 400 mV and fluctuated between 2 and 4.2 within the 400–520 mV range. The researchers attributed these fluctuations in current activity as well as pH within the 380–400 mV range to metastable pitting events due to the dissolution of MnS inclusions. The corresponding change of pH and electrical activity as a function of corrosion progress was clearly identified. According to the scientists, this research is capable of expanding transient and highly localized studies of corrosion events.

JUNE LAU

SHG Utilized as Nondestructive Method of Buried Corrosion Detection

The use of second harmonic generation (SHG) signal as a means of corrosion detection for bodies coated with paint has been demonstrated by a group from the Departments of Physics and of Electrical

Engineering at City College of New York. While scientists desire the ability to detect the onset of corrosion underneath layers of paint, current nondestructive methods are limited. As reported in the August 15 issue of *Optics Letters*, such a task is made possible by the use of a focused laser in the near infrared region to map out a 2D/3D corrosion profile.

The output of a modelocked Ti:sapphire laser, with an 810 nm wavelength, 120 fs pulse duration, and 76 MHz pulse repetition rate, was used to scan the volume of a coated-uncorroded, an uncoated-corroded, and a coated-corroded sample. The incident optical beam is focused with a 20X lens (Numerical Aperture 0.4) providing a focal spot of ≈ 10 μm extent. The SHG signal is a backreflected signal, redirected back through the same lens, through a beam splitter, and into a photomultiplier tube and depends critically on the position of the focal volume with respect to the various layers sampled. The corroded samples consisted of blocks of iron exposed to open air. The uncorroded sample was hand polished. A 30-μm thick layer of paint was painted onto one corroded and the uncorroded sample. Of the painted, rusted, and metallic iron samples, the surface paint layer generated the largest SHG signals and the metallic iron generated the least. By using signal contrast and a computerized motor translation stage to control the lateral and longitudinal position of the focused laser spot, a 2D/3D map of the system profile could be generated. However, the paint transmission characteristic was only 0.09% within the spectral range of 400–800 nm. The scientists suggest adapting different light sources for different types of coating in order to maximize transmission to the underlayers. This work provides a new means of early corrosion detection for aircraft, structures, and other industrial equipment.

JUNE LAU

Electrochemical Reduction in Alkaline Electrolyte Removes CuS Phase to Form CuInS₂-Based Solar Cells

A team of researchers in the Solar Energetics division of the Hahn-Meitner-Institute (HMI) in Berlin, Germany, has reported a method for the removal of unwanted CuS from the surface of CuInS₂-based photovoltaic cells. Instead of the traditional cyanide washing, a straightforward electrochemical reduction in an alkaline electrolyte and subsequent dissolution are employed, leading to complete removal of the covellite (CuS) phase and a photoactive CuInS₂ material.

Thin film solar cells based on CuInS₂ are promising materials for large-scale applications, as they show high performance at low production costs. CuInS₂ has a high absorption coefficient and a bandgap energy around the maximum of the solar spectrum. "However, there are several problems that hinder the further development", said H.J. Lewerenz, professor at the HMI. "A cyanide etch is used to remove the unwanted covellite phase from the surface, a poisonous CdS layer is implemented and this results in a band II lineup leading to reduced photovoltages."

As reported in the September issue of *Electrochemical and Solid-State Letters*, the films are prepared by sequential sputtering of the metals with a copper-to-indium ratio larger than one and subsequent annealing in a sulfur atmosphere. During the annealing process, CuS, which is a *p*⁺-type semiconductor, is formed on the surface of the grains and needs to be removed. The only process that selectively attacks the CuS while leaving the CuInS₂ intact is a cyanide etch.

"We have now found a possibility to clean the grain surfaces from CuS without using a cyanide solution," said U. Störkel, who is working on a postdoctorate with Lewerenz. "The disappearance of CuS-related features in cyclic voltammograms recorded in 0.1 M K₂SO₄ at pH 10 suggested that the covellite phase might dissolve during electrochemical cycling in alkaline K₂SO₄ solution at potentials between -0.9 and -1.2 V versus saturated calomel electrode or SCE." The current versus time behavior at fixed potentials in this range showed that the number of charges that had flown was proportional to the excess of Cu used in the preparation of the films. X-ray diffraction confirmed the complete removal of the covellite phase and gave evidence for the formation of small amounts of Cu_{2-*s*}S. Scanning electron micrographs before and after cycling demonstrated the removal of most surface species from the polycrystalline CuInS₂.

"We believe that the CuS is reduced starting at about -0.9 V," said M. Aggour, a senior lecturer at the University Mohammed V in Rabat, Morocco, and regular visiting scientist at the HMI. "Cu₂S can exchange anions with the solution resulting in surface bound Cu(I)(OH)_s. These species can undergo a redox reaction with water to form water soluble Cu(OH)₂ and hydrogen. The gas evolution is visible to the naked eye even at -0.95 V."

His collaborator, Joachim Klaer, said, "It is, of course, also possible that partially reduced copper species or copper metal are formed. We saw small amounts of Cu_{2-*s*}S in the XRD [x-ray diffraction]

patterns. There are no copper peaks visible, but we cannot exclude the presence of a small amount. That is the reason for our planned synchrotron experiments—the high energy resolution will allow us to distinguish Cu^0 , Cu^+ , and Cu^{2+} easily.”

The electrochemically treated materials show significant photocurrent starting at -0.49 V during scans toward more negative potentials and up to -0.32 V in the backwards scans. The photocurrent is smaller than that of KCN-etched samples. “This might be due to the presence of a thin Cu_2S layer or residual copper,” said Störkel. “We are currently working on the transformation of Cu_2S into stoichiometric CuInS_2 using, for example, alkaline solutions containing In^{3+} ions.”

CORA LIND

Third-Body Interfacial Layers Reduce Wear of Dental Glass-Ceramic Surfaces

An understanding of the mechanisms of wear between restorative dental glass-ceramic interfaces is important in the development of new, wear-resistant dental materials. Ideally, experiments should simulate the conditions inside the mouth during chewing, where debris layers formed between the teeth are flushed away by saliva and the sliding motion of the contacting surfaces, preventing the formation of a stable, third-body interface. Researchers Attota Ravikiran and Said Jahanmir of the Ceramics Division of the National Institute of Standards and Technology (NIST) compared the wear of surfaces that were continually flushed with fresh distilled water with those whose surfaces were not flushed during controlled grinding to elucidate the nature and importance of the third-body interface. Their results are reported in the July issue of the *Journal of the American Ceramic Society*.

Blocks of Dicor MGC (from Dentsply), a tetrasilic fluoromica compound containing mica platelets with an average diameter of $2\ \mu\text{m}$, were polished to an average surface roughness of 5.6 ± 1.2 nm using diamond pastes. High-purity (99.5%) alumina balls with a Vickers hardness of 14.7 GPa were fashioned into a pin-on-disk type of tribometer. The alumina balls were ground against the polished faces of the Dicor MGC at loads varying from 5 to 30 N along wear-track diameters of 6.5 and 9.5 mm, with the contact surface submerged in distilled water at all times. In one set of tests (the “flushing” experiments), the contact surface was continuously flushed with fresh distilled water during the entire sliding

period; in the “nonflushing” experiments, the original water was retained throughout the experiment, so that the surfaces were not cleaned of debris.

Subsequent measurement of wear volumes revealed that the flushed surfaces wore more heavily than the nonflushed surfaces. This result indicates that accumulation of third-body wear debris at the interface of dental ceramics acts as a protective, load-carrying film that separates the primary contact surfaces and thus reduces wear. In the absence of such an accumulation—when the interface is

flushed—the dental ceramic itself is subject to greater degrees of deformation and fracture. The researchers suggest that experiments utilizing a flushing technique simulate actual oral conditions more closely, and might give more meaningful data in future investigations.

TIM PALUCKA

Sputtered Co/Ti Film Directly Oxidized Forms High- κ CoTiO_3

A high-quality, ultrathin, high- κ cobalt-titanium oxide (CoTiO_3) dielectric was recently reported in the September issue

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