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Investigation of Scanning Kelvin Probe Techniques

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Abstract

The original scope of this work was to advance the understanding of corrosion properties of additively manufactured (AM) materials by correlating microstructural defects in AM materials to the material conventional counterparts utilizing a scanning kelvin probe [Ametek VeraSCAN Electrochemical System]. However, upon the initiation of project research, it was observed that the system was not operational due to unknown hardware and software problems. The evolved scope of this work was to reconcile the operational issues and develop a repair and mitigation plan. After extensive troubleshooting, it was determined that the software was not properly configured, and the electrometer had permanently malfunctioned. A repair plan was developed, with identified malfunctioning components, with a manufacture quoted $2,152.50 repair cost. Several mitigation steps are also recommended, to avoid additional issues and hardware concerns. With the successful repair and use of the VeraSCAN system, the university will greatly benefit from the full functionality of this electrochemical system. If the stated plan is executed, future students will be able to successfully complete the original scope, and benefit the Corrosion Engineering Program, and Department of Chemical and Bimolecular Engineering.

Executive Summary

Problem Statement

The original purpose of this project was to advance understanding and insight into the corrosion properties of additively manufactured (AM) materials by correlating microstructural defects in AM materials to their inherent corrosion performance properties, utilizing the scanning kelvin probe technique. Applications of the laser powder-bed fusion (LPBF) additive manufacturing technique are ever expanding and show promise in revolutionizing numerous manufacturing industries. However, the high-temperature and unique cooling rate effects associated with this process create substantially different microstructures in AM materials, creating unique metallurgical and electrochemical properties. Unexpectedly, the VeraSCAN Electrochemical Scanning Base System, located at the Engineering Research Center (ERC), was non-operational, due to several complications. The work of this project evolved to diagnose and repair the complications and provide an insightful guide for future projects which choose to utilize the VeraSCAN. Subsequently, this work would serve to promote usage of the VeraSCAN, and the scanning kelvin proves technique for the Corrosion Engineering Program, college, and students.

Summary of Results

The development of a beneficial operations manual, not provided with the manufacturers software, is provided herewith, with insights provided from previous co-op rotations. Discussion is included to assist future projects with understanding and analysis of results, as well as discussion of possible applications for the scanning kelvin probe technique. Malfunctioning parts were diagnosed and identified, and software was optimized for future use. The VeraSCAN Electrochemical Scanning Base System has numerous electrochemical investigation capabilities, and the proposed repair plan encompasses the usage of all installed capabilities. This repair plan was identified to ease future complications and maximize utility to the Engineering Research Center.

Conclusions

Initial work was completed independently, however; with assistance from Ametek, the malfunctioning component was identified to be the electrometer. Testing revealed that the piezo electric, nor the lock-in amplifier were the source of the feedback error. The electrometer is unable to be repaired in-house and is required to be sent to Ametek for full repair and/or replacement. Additional components are recommended to maximize the utility of the VeraSCAN Electrochemical Scanning Base System, that were not available at the time of this work.

Implications

The identification and repair of the VeraSCAN Electrochemical Scanning Base System benefits the Corrosion Engineering Program, and department. Additionally, the future availability of the equipment, and subsequently the scanning kelvin probe technique, provides a powerful resource for future students who wish to conduct research utilizing the SKP or scanning vibrating electrode technique (SVET). The honors project experience has benefitted me greatly in understanding the difficulties and roadblocks often experienced in research. Importantly, this project has allowed me to utilize analytical skills, in diagnosing the complication occurred during this project. The repair of this equipment is essential for future research projects, and the execution of the original proposal by a future honors student.

Recommendations

The repair of the VeraSCAN Electrochemical Scanning Base System is recommended for the execution of the original research proposal. The purchase, or acquisition, of additional components will enhance the capability of the VeraSCAN, and aid in additional electrochemical and material research. Specifically, the acquisition of an optical surface profiling (OSP) laser will greatly enhance the accuracy of measurements and remove potential operational errors. It is further recommended that this project be assigned to a younger undergraduate student, for a long-term, comprehensive project approach.

Introduction

The original scope of the project involved advancing understanding and insight into the corrosion properties of additively manufactured (AM) materials by correlating microstructural defects in AM materials to the materials' inherent corrosion performance properties. Through this project, scanning kelvin probe techniques were to be used to investigate these electrochemical and metallurgical properties. Throughout previous co-op research projects, a unique understanding of the SKP technique, and the intricacies involved in sample calibration, provided insight into the original project scope. However, due to unforeseen operational issues, the original project purpose evolved. The scope of this work changed to encompass the diagnosis, troubleshooting, and repair of the VeraSCAN Electrochemical Scanning Base System located at the Engineering Research Center (ERC).

The bulk of this work revolves around the identification of non-operational components, a work-plan to reconcile operational issues, and the identification of applications, suggestions, and guide for future research projects. The SKP is a powerful, non-destructive technique, capable of identifying discrete material, electrochemical, and metallurgical properties in conductive materials, across a variety of applications. The work of this report, as well as a repair-plan for the VeraSCAN machine, will greatly benefit the program, college, and future students who wish to conduct research projects utilizing the SKP technique.

Background

In many applications, non-destructive evaluation (NDE) is a necessity for adequately assessing electrochemical and material properties. The scanning kelvin probe (SKP) is a powerful electrochemical analysis technique, uniquely capable of operating in open-air environments, across of variety of materials. SKP is a non-contact technique, utilizing a lock-in amplifier to measure sample electrode potentials, and subsequently corrosion potentials by determining the contact potential difference (CPD) between a reference probe and sample surface [1]. Numerous advantages are demonstrated by the SKP technique, including:

1. Determination of localized corrosion under (in)organic non-conducting films [2,3]
2. Non-contact electrode potential measurements, and corrosion potential correlation
3. Identification of sub-surface defects and microstructural changes [4]

Conversely, there are several limitations to the scanning kelvin probe technique, including:

1. Sensitivity to surface preparation, morphology, and contaminants
2. Timely data collection periods per unit time
3. Subjectivity of data collection and analysis

The scanning kelvin probe technique ascertains the corrosion potential of a sample via determination of the work function. Work function is defined as the sum of the inner chemical potential of an electron, and the energy required to move such electron across the interface of the sample. The scanning kelvin probe technique, illustrated by Figure 1., consists of a connected circuit-system, with an integrated lock-in amplifier [1].

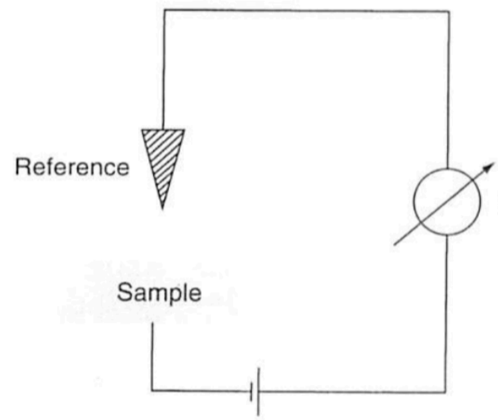

Figure 1. Schematic representation of the SKP technique

A probe is positioned within 100 μm from the sample surface, thus forming a capacitor, with the ambient environment acting as a dielectric. A piezo electric is utilized to vibrate the probe (on the order of 1-30 μm,) with a potential applied sufficient enough to minimize the capacitance between the two samples. This capacitance, known as the "nulling potential" is recorded and correlated with the E_{corr} of the sample.

The VeraSCAN Electrochemical Scanning System is an advanced electrochemical workstation, capable of executing several relevant techniques. Of relevance to the stated work, the scanning kelvin probe (SKP) technique and the scanning vibrating electrode technique (SVET) are vital capabilities for electrochemical analysis. The SVET uses an individual probe to measure potential field gradients in solution, providing *in situ* analysis of degradation processes. Combined with the SKP technique, these methods provide a powerful experimental approach to understanding corrosion properties of additively manufactured (AM) materials.

Experimental Procedures

Suggested Sample Fabrication

Samples are to be cross-sectioned using an abrasive cut-off wheel to produce a smooth surface perpendicular to the weld. Metal flags are to be fashioned for mounting in 2.5 cm diameter epoxy mounts. Samples prepared for scanning kelvin probe examination are to be ground in successive grits using SiC paper, utilizing a rotating metallographic polisher. Samples are to be ground down to 1200 grit size. Samples are to be thoroughly cleaned in an acetone beaker in an ultrasonic bath and dried in a dry air stream.

Suggested Sample Preparation

Samples are to be thoroughly cleaned before scanning kelvin probe examination, utilizing organic solvents to ensure complete removal of particulates and/or oils. Gloves are to be utilized to prevent surface exposure to oil and other particulates. Samples are to be thoroughly cleaned with an acetone wash, isopropanol wash, and methanol wash, dried in dry air stream. Before initiation of experiment, sample is to be thoroughly cleaned with canned air.

Suggested Scanning Kelvin Probe Operation

A suggested operation process for effectively utilizing the scanning kelvin probe technique is presented. Once sample fabrication and preparation are conducted, completed samples are to be placed on the VeraSCAN stage. Software procedures, and ancillary tasks are included in the manufactures manual. The below suggested operation supplements manufacturers resources.

1. Positioning of Sample

   The test sample should be placed in the tri-stand stage, Figure 2, with sample placement centered on the VeraSCAN platform. Probe control should be validated before experimental leveling, ensuring adequate dimensions of motion in the y-direction and x-direction.

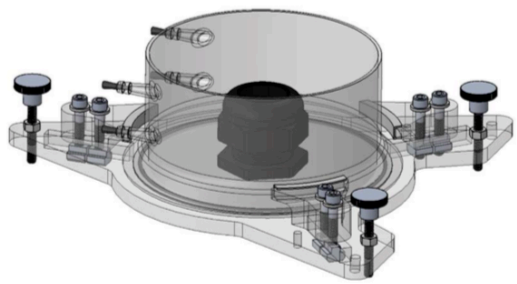

Figure 2. Diagram of tri-stand schematic

2. Leveling of Sample

   A leveling compass, included with equipment, should initially be utilized to qualitatively level the sample, vary heights using the pegs on the tri-stand base. After leveling, the capacitive height measurement (CHM) technique should be used to quantitatively level the sample. Using the CHM technique, consecutive line scans should be conducted across the sample, adjusting the tri-stand heights appropriately to achieve a constant height across the work area. Critically, the line scan height measurement test must be conducted in the x-direction and y-direction, ensuring sample levelness. This step is essential, as the SKP technique is sensitive to changes in working distance (probe-to-sample distance).

3. Height Verification

   After leveling of sample, the working distance should be verified. The probe tip is lowered until probe-sample contact is made, indicative of a soft “clicking” sound. Great care must be taken in conducting height verification. The probe tip is lowered in 10 µm steps, until surface contact is close. Probe contact should be monitored using the included camera, lowering steps to 1 µm distance until “clicking” sound initiates. Subsequently, the probe should be automatically raised 200 µm in the z-direction. Height calibration is verified by ensuring the system acknowledges the probe is 200 +/- 1 µm from the surface.

4. Signal Calibration

For proper signal calibration, the probe must be centered over the sample, 80-100 µm from the surface. A “Measurement” reading will populate on the prompt, Figure 3. Initially, this measurement will sporadically vary. The “Ref Phase” must be adjusted to until a “No reading” measurement is attained, ensuring the lock-in-amplifier is in-phase with the applied potential. Subsequently, the “Ref Phase” is adjusted +90 degrees out of phase with the reading. Signal attenuation should be between 10-30 mV.

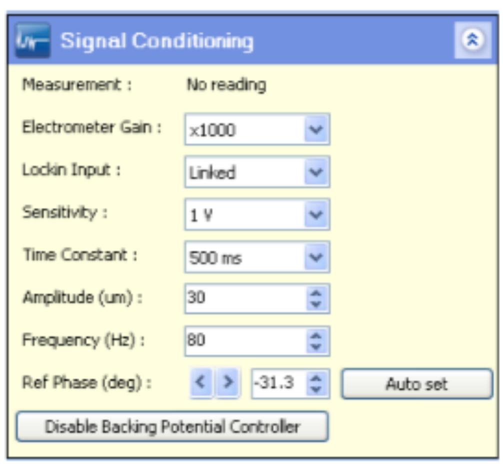

Figure 3. Signal Conditioning Prompt in VeraSCAN software

5. SKP Test

   After completing verification and calibration of the system, the SKP technique can be conducted. Due to the nature of the CHM technique, the sample is charged (to a potential of 10V) and must be allowed to discharge. It is suggested that a sequence of SKP scans are conducted, to quantitatively determine state of discharge.

Scanning Kelvin Probe Repair Process

The work of this project revolved around the troubleshooting, diagnosis, and repair of the VeraSCAN Electrochemical Scanning Base System, located in ERC 214C. Initial work revolved around updating the Ametek software, reconnecting the system for operational use. Initial work took approximately two weeks of work, with removal of rust from the VeraSCAN platform, organization of components, and updating of system software and firmware.

Initial concern was related to cabling issues experienced in late Fall 2017 semester. A missing BNC-to-Alligator clip cord was identified, responsible for connecting the sample to the DAC lock-in-amplifier unit. A replacement cord was purchased and verified electrical connectivity before winter recess.

However, initial non-operational issues were identified the first week of Spring 2018 semester. Upon configuring the scanning kelvin prove for initial experimentation, an error message displayed, Figure 4.

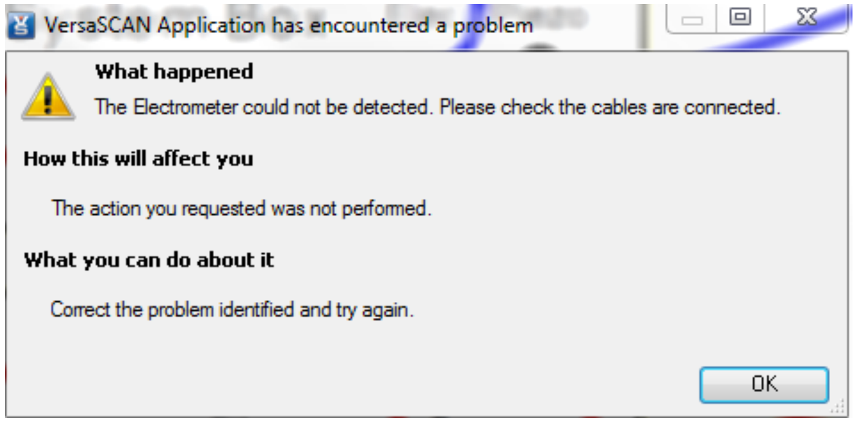

Figure 4. Error message displayed by VeraSCAN

This message indicates the failure of the electrometer to respond to software commands. Initially, this error was attributed to user error, a failure in software configuration and/or experimental set-up. The entire system was disassembled, and cords were separated to efficiently organize the VeraSCAN cabling. Upon reorganization, the system error remained. Following guidance from Ametek, software and firmware were clean installed, with direct downloads provided by Ametek support. The system error persisted through all repair efforts. Of concern, the locking mechanism on the 500-µm scanning kelvin probe was unaligned. The 250-µm scanning kelvin prove was implemented, and the error message persisted. After extensive troubleshooting, Princeton Applied Research (PAR) was contacted for additional support. PAR identified possible cabling issues, related to non-connectivity of BNC cables. This was determined to not be the cause of the system error, as spare cables were substituted to ensure connectivity. After additional communications, it was determined to be an electrometer failure, with repair and/or replacement suggested by the manufacturer. Follow-up with Ametek conducted at the NACE CORROSION 2018 conference in Phoenix, AZ, with attached quotes for specific components is presented.

Results and Discussions

Guidance Moving Froward

It is recommended that the repair of the VeraSCAN be implemented, as the machine will provide increased benefits for the department and university. The original project scope is still valid, and should be afforded to a younger undergraduate student, capable of undergoing a multi-year experimental approach. A repair schedule was fashioned, with relevant information identified from the work of this project. The repair or replacement of the electrometer, seen in Figure 5. is vital and must be conducted for the successful operation of the system. An additional component is recommended for purchase, as the part would maximize the utility of the system, as well as provide advanced additional capabilities for the system.

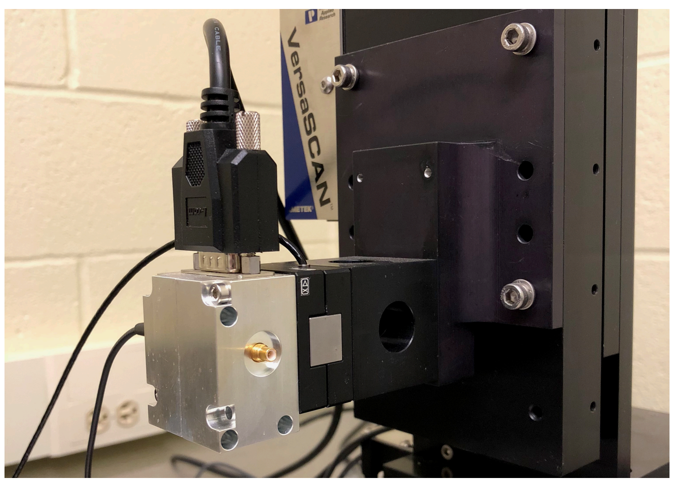

Figure 5. Electrometer, piezo vibrator, VeraSCAN assembly

Repair Cost Estimates

The quoted repair costs from Ametek are provided in Table 1., totaling $2,152.50. The electrometer is the vital component in need of replacement, for complete operation of the VeraSCAN. This component is easily installed by a campus technician and will not require on-site technical support. The SKP calibration sample is highly recommended for purchase, as the sample will prove to be an essential tool for students to use while acclimating of the scanning kelvin probe technique. The sample, a galvanized steel sample with a zinc-core, provides a quantifiable, defined work function region for sample analysis. An additional BNC cord is suggested for replacement for the DAC-to-Sample connection.

Table 1. Required Component Costs

Component	Part #	Cost ($)
Electrometer	224077	1,597.50
Calibration Sample	224116	535.00
BNC Cord	233918	20.00

Additionally, the SVET technique is a unique capability of the VeraSCAN. The current SVET probe is malfunctioning, and replacement of the probe would provide additional electrochemical insight into the original project hypothesis, Table 2.

Table 2. Optional Component Costs

Component	Part #	Cost ($)
SVET Probe	224111	906.00

Similar to SKP probes, SVET probes are extremely delicate, and require delicate care and attention. Moving forward, significant attention should be placed on storage and operation of the

VeraSCAN and associated probes. Correct storage of VeraSCAN probes is critical to long-term operational capability. SVET probes are sensitive to storage conditions and shall be correctly stored in manufacture-provided probe containers. Additionally, SKP and SVET probe-to-sample contact is detrimental to the accuracy and integrity of the probes. Sample contact “crashing” should be avoided, as irreversible damage is often experienced.

Conclusions

Although difficulties occurred in fulfilling the original project proposal, the current work has progressed to effectively serve the college and program, by identifying malfunctioning components, and presenting a plan to repair the VeraSCAN Electrochemical Scanning Base System. The electrometer was determined to be non-operational and requires repair. Preliminary quotas from Ametek indicate that it will cost $2,152.50 to fix the VeraSCAN Electrochemical Scanning Base System, with an additional $906.00 required to bring the additional SVET capability back to the equipment. The expanded use of this system will greatly benefit NCERCAMP, faculty, and other undergraduate research assistants. Additionally, the assignment of this research project to a younger undergraduate student will allow for a more comprehensive experimental investigation, over a multi-semester time interval.

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