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Novel Probe Designs for the Scanning Kelvin Probe System

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Abstract:

The tungsten wire probe (0.5 mm diameter), has been shown to be the most suitable to be used with the SKP100E system in giving reproducible accurate measurements. The probe is least height dependent of the other probes. It has a better linearity on the calibration data and the measurement-to-measurement variation is minimal.

Keywords: *Scanning Kelvin Probe (SKP), Volta potential, EMF, Parallel Plate Capacitor, Work Function, Kelvin Potential*

Introduction

Lord Kelvin [1] in 1897 presented his work at a meeting of the Royal Institute and described the principles behind the Kelvin measurement of Volta potential for the first time. When two dissimilar electronic conductors are in contact, electrons flow from the material that is less noble to the one that is more noble until equilibrium is reached and the contact potential V_c is formed at the junction. He showed that a simple electrical circuit could be constructed from a pair of metals. The ends of the two metals are arranged to form a parallel plate capacitor. An electric field is generated between the two plates, which is the result of the spontaneous separation of electrons. In the case of a copper / palladium junction, the copper plate becomes positively charged and the palladium negatively charged. A galvanometer and a battery placed in series complete the circuit. As the distance between the two plates is periodically changed, the galvanometer registers an alternating current, which is the result of mechanical vibration of the two plates in an electric field.

A compensating voltage from a variable source is then applied until the electric field is nulled out and the galvanometer registers zero alternating current. This instrument is known as the Kelvin method for measuring the Volta potential. The Volta potential is obtained by plotting a graph of electrometer deflections against the applied potential difference. The intercept on the axis along which is the potential difference is plotted will be the contact EMF.

Zisman [2] improved the Kelvin probe greatly; he vibrated one of the electrodes continuously, instead of only displacing it in one direction. This development led to easier amplification of the signal and its detection by oscilloscopes or phase - sensitive detectors.

Refinements to the method continued as researchers improved the means for electronic detection and for vibrating the electrodes. Delchar [3] and Blott [4] described methods in which the ac signal was rectified and the resulting dc signal fed back continuously to balance out the Volta potential. This was used for improved stability and for automatic recording of changes in the Volta potential. Various methods of vibrating the electrode have also been studied: e.g. mechanical methods by Harper [5], electrochemical methods by Hopkins [6] and Parker and Warren [7]. Surplice [8] made numerous modifications to the system to produce a flow of charge in the circuit by modulating the capacitance. They investigated the effect of stray capacitance by varying the spacing and amplitude of vibration of the Kelvin probe and the potential of a screen inside the vacuum chamber. These measurements, however, were mostly preferred with the vibrating electrode connected to the high impedance amplifier and coarse effects were involved. Previous designs had problems with moving one electrode in vacuum and suffered from the effects of stray capacitance.

Craig and Radeka [9] tried to avoid modulation of stray capacitance by shielding the vibrating high impedance probe from the surroundings (except the sample surface) by a low impedance guard electrode, which was electrically isolated from the probe and rigidly connected to it, and vibrating with it. This method also eliminated the effects of the side faces of the sample. However, it is less adequate for the investigation of small or irregularly shaped samples. Moreover, in spite of the rigid connection, the capacitance between the probe and the guard may be modulated considerably due to the changing position relative to the sample surface. Any local difference in work function between probe and guard may therefore cause an erroneous signal on the probe. De Boer [10] described procedures for making Kelvin measurements with arbitrarily shaped electrodes which eliminated the effect of stray capacitance caused by shielding the vacuum chamber, and which made it possible to detect the combined influence of parts of the sample electrode with a different work function than the surface under study.

Ritty [11 – 12] developed an improved method to measure the backing voltage. They showed that it was advantageous to detect the current rather than the usual voltage detection. A mechanical driving mechanism was designed similar to that of Parker and Warren [7]. A novel theoretical analysis, based on plane capacitors, was developed and they showed that it was misleading to attempt to measure the Volta potential corresponding to a perfectly defined surface without setting a guard shield around the reference electrode. With incorporation of an automatic data acquisition system this led to improved sensitivity and reliability.

A complete computer controlled Kelvin probe was developed by Baczynski [13], which led to the development of a commercial Kelvin probe system. Reducing the size of the vibrating reference electrode increased the spatial resolution of the Kelvin measurement. Further, the probe could be guarded so that capacitive coupling of the probe to other surfaces in the environment that led to substantial errors in measurement, is substantially reduced [14]. Also, the adsorption of gases on to the probe surface could affect its work function. This was overcome by heating the probe to flash off adsorbed gases. It was also shown that cleaning of the probe gave more reproducible results.

Atanasoski [15] calibrated a dry redox couple (Ag/AgCl), as a reference material for the Kelvin probe in humid environments. The experiments carried out showed it to be very useful for corrosion studies. The Kelvin probes developed varied in design and metals used. The design took into consideration the type of environment used for the measurement, the types and sizes of samples used and the system considerations. The overall aim was to produce a Kelvin probe to give good sensitivity, to be robust, easy to handle, could be used in different environments, easy to clean and remake. The Kelvin probe is a fundamental part of the system as it takes the measurement. The theory of the Kelvin probe has been discussed in Chemistry and Physics handbook [16]. Several techniques with enhanced spatial resolution have been introduced recently to the field of corrosion science, with the advantages of giving information on the processes occurring locally at electrochemically active surfaces. The SKP [17 – 30] has been quite successful.

EXPERIMENTAL

The Volta potential difference is related to the electrochemical or corrosion potential in a linear manner, however, a calibration constant is needed in order to calculate the electrode potential from a Volta potential measurement. For aqueous electrolytes, the calibration constant is easily obtained by measuring the Volta potential of a metal electrode which is exposed to an electrolyte containing the metal cation in a defined concentration [31 – 34]. Then the electrode potential of the metal/metal cation system is known from the Nernst equation and the calibration constant is obtained, e.g., by plotting the known electrode potential versus the Volta potential for different metal/metal cation systems. However, it should be kept in mind that the calibration constant contains the work function of the reference metal and depends strongly on the actual surface condition of the reference material. The calibration procedure has therefore to be performed frequently and typically only with one simple metal/metal cation system e.g. $Cu/CuSO_4$.

INSTRUMENTATION

The Kelvin current is used to obtain the Volta potential signal. The current appears because in the local capacitor formed by the tip and the sample under study, the tip is vibrating. The tip is made from a material with a known work function. A current measurement device (**Figure 1**) connects both 'parallel plates' of the condenser.

When the equilibrium of the Fermi level is established between the tip and a sample, a Volta potential appears between the 'plates' (V), and the capacitor is charged. If the distance between the parallel plates is changing, the capacity is altering, and due to the constant voltage between the plates, the charge on the plates (ΔQ) changes too. This charging process causes a current in the measurement device, the Kelvin current. If the Volta potential is compensated by a variable voltage source inserted into the circuit (V_0), there will be no current flowing in the circuit. The voltage of the source now equals the Volta potential difference value [16].

Design of Probes

*Stainless Steel Probe (1.*6mm *Diameter)*

A 'standard' probe consisted of a hollow copper tube (55x5 mm) and a 0.5 mm wall thickness at the end of which was held in place a 5 mm length of 316 stainless steel rod (1.6 mm diameter). The hollow tube was tightened around the stainless steel rod and the 316 stainless steel rod protruded 1 mm from the tube. An electrical pin connector was used to electrically connect it to the scanning head of the SKP system. A thin flexible (50 mm in length) electrical wire was used to make an electrical connection to the 316 stainless steel rod to pin 3 of the connector which was for the measured signal. Another thin flexible electrical wire (10 mm in length) was used to connect the hollow tube to pin 1 of the connector, which was the driver shield connector.

Gold Rod Probe (2 mm Diameter)

A gold rod (60x2 mm) was encased in glass, a copper braid screen (50 mm in length) was placed over the glass. Electrical connections were carried out as before and checked. A 50 mm in length clear PVC heat shrink sleeve was used to cover the length of the copper braid screen. The last 10 mm in length of the gold rod encased in glass was ground to an acute angle around the 2 mm diameter of the gold rod using 120-grade silicon carbide paper. The surface of the gold rod was ground with 600, 800 and 1200 grade silicon carbide paper then rinsed with de-ionised water, acetone and left to air dry.

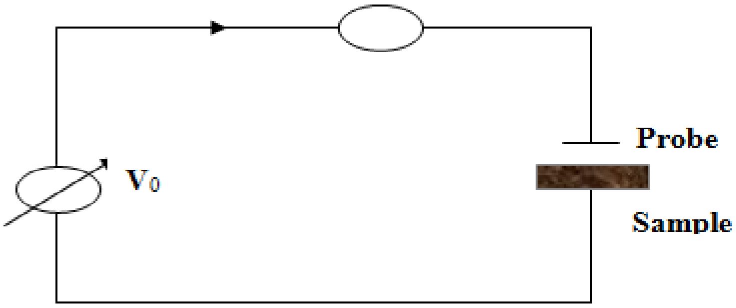

Fig. 1: *Principle of Volta Potential Compensation and Measurement of the Kelvin Current.*

Copper Wire Probe (1 mm Diameter)

A plastic tube (27 mm) was used at the centre of which a copper wire (27 x 1 mm diameter) was held in place. A copper mesh surrounded the tube and around the mesh PVC heat shrink was also used. The surface of the exposed wire was ground using different grit sizes of silicon carbide paper, as carried out previously and then connected to the SKP system.

Platinum in Glass Probe (0.5 mm Diameter)

A glass tube was drawn down onto a platinum wire (60x0.5 mm diameter) and covered with a 55 mm in length copper braid screen, over which was, placed black PVC heat shrink sleeve. Finally, the exposed Pt disc was ground flat to 1200 grit finish.

Tungsten Wire Probe (0.5 mm)

A tungsten wire (20x0.5 mm) (Goodfellow metals) was anodised in 5%H_2SO_4, the voltage was slowly adjusted to a maximum of 20 volts. The current decreased to a low value after several minutes and the tungsten wire became yellow on the outside due to oxide formation. It was important to ensure that the tungsten wire was straight and not at an angle. A solid micro-metal rod (20 mm in length and 7 μm in diameter) was fixed and clamped into a lathe and drilled out leaving 2 mm at the sides of the rod. The micro-metal was then placed over the tungsten wire to act as a driver shield. A 15 mm in length black PVC heat shrink sleeve was used to cover the length of the micro-metal rod. The end surface of the tungsten wire was ground with 800 and 1200 grade silicon carbide paper, rinsed with de-ionised water, and acetone and left to air dry. After assembly, the tip protruded about 0.5 mm from the micro-metal shield.

Potential Step Electrodes

Samples of copper rod, iron rod and stainless steel rod were used to make potential step electrodes for calibration of the SKP. Two pieces of each metal rod (5x5 mm) were separated by a section of double-sided nylon tape (Sellotape GB Ltd.); care was taken to ensure that there was no contact between the metals. A 25 cm length of flexible electrical wire was then soldered to one of the rod pieces and another 25 cm length of flexible electrical wire was soldered to the other rod piece. The electrode was placed into a slightly greased MetSet cylindrical mould into which was added Araldite resin and hardener. The epoxy resin was left for 24 hours to allow complete curing. The top surface of the specimen was ground with 330, 400, 600, 800 and 1200 grade silicon carbide paper. In step scan mode, area and line scan maps were carried out using SKP system. Subsequent scans were performed under identical parameter values. The height was set using Topography mode. Different potentials were applied to the electrode and the step potential at the junction was measured with the probe.

Ecorr Measurements

The corrosion potentials of various metals were measured against a standard calomel electrode Ag (99.97%) (Advent research materials Ltd.), Cu (99.99%) (Good fellow metals), Fe (99.99%)(Good fellow metals), Ni (99.99%)(Good fellow metals), and Zn (99.99%) (Good fellow metals) at room temperature ~19.2^{o}C. The electrolytes used comprised of 0.5 mol. dm^{-3} solution of the relevant metal sulphate (nitrate in the case of Ag).

Kelvin Potential Measurements

Cu, Fe, Ni, Zn and Ag coupons were used to obtain Kelvin potential measurements. The top surface of the specimens were ground with 600, 800 and 1200 grade silicon carbide paper, rinsed with de-ionised water and acetone. The coupons were kept in a desiccator prior to use. A square well was made in the centre of the coupons using PVC tape. The specimen was placed on a laboratory jack (Merck UK Ltd.), which acted as a sample holder. The specimen was checked to be horizontal, flat and parallel to the probe. This was achieved by using a spirit level placed at various points on the instrument and on the sample. The well in the centre of the specimen was filled with a 0.5 mol.dm-3 aqueous solution of the respective metal sulphate (0.5 mol.dm-3 nitrate salt in the case of Ag).

Then visually the Probe was brought as close as possible to the meniscus of the aqueous solution making sure there was no contact with the solution. The probe was brought 50 μm vertically up from the meniscus. Thus, the E_{kp} value was obtained with the vibrating reference probe consistently positioned 50 μm above the electrolyte meniscus in the centre of the well. The system was allowed to equilibrate before the measurement was taken.

The vibration amplitude of the probe was 25 μm and subsequent readings were performed using the same height and vibration amplitude. A thin clear plastic sheet (0.05 mm thickness) was rinsed with de-ionised water and acetone, placed over the well containing 0.5 $mol.dm^{-3}$ aqueous solution of the respective metal sulphate (0.5 $mol.dm^{-3}$ nitrate in the case of Ag) solutions. Visually the probe was brought as close as possible to the thin clear plastic making sure there was no contact with the plastic. The probe was again brought 50 μm vertically up from the thin plastic sheet. The E_{kp} value was obtained with the vibrating reference probe positioned 50 μm above the thin plastic sheet. The system was allowed to equilibrate before the measurement was taken.

Height Dependence Measurements

Coupons (35x35x2 mm) of iron (99.99%) were used for this calibration. The top surface of the specimen was ground with 600, 800 and 1200 grade silicon carbide paper, rinsed with de-ionised water and acetone. A square well was made in the centre of the coupons using PVC tape. The specimen was checked to be horizontal and flat via a spirit level and the square well was filled with a 0.5 $mol.dm^{-3}$ aqueous solutions of the respective metal sulphate. Visually the probe was brought as close as possible to the meniscus of the aqueous solution making sure there was no contact with the solution. The probe was brought 50 μm vertically up from the meniscus. The E_{kp} value was obtained with the vibrating reference probe positioned 50 μm above the electrolyte meniscus in the centre of the well. The system was allowed to equilibrate before the measurement was taken. The probe was moved vertically up in 50 μm increments and the reading was taken again, for the new height from the meniscus.

RESULTS AND DISCUSSION

The graphs plotted for the probes are a calibration graph (Kelvin potential measured with the probe against the corrosion potential vs. SCE), and a height dependence and variance plot (Kelvin potential measured with the probe against the height from the sample).

Various metals have been shown to be suitable by other authors as a probe for a Kelvin measurement. Stratmann [35] and Williams [36] have used gold wire as the reference material and shown it to give accurate and reproducible values. Hansen [33] has used stainless steel because it is inert to many materials. Danyluk [14] used tungsten to produce a probe and showed it to be a suitable material to use as a reference probe. Platinum wire is generally used in electrochemical probes e.g. Scanning Vibrating Probe (SVP) technique [37] as it is relatively noble. The common properties that these share that make them good materials are that they are relatively inert, oxidise slowly or not at all so that their value stays constant over time. These materials are also easy to handle and easily cleaned, which has been shown by authors to improve results [14].

When taking any measurements with the designed and developed probes certain precautions were taken to make certain that meaningful and true values were obtained.

- The probe tip was cleaned.
- Ground flat and made sure that it was parallel to the sample it was measuring.
- The samples were kept in a dessicator after polishing and only taken out when used for the measurement.
- The samples were handled as little as possible so as not to contaminate the surface affecting the measured value.

Various factors are also understood to affect the measured signal.

- Stray vibrations
- Magnetic coupling
- Electrostatic coupling
- Probe tip contamination
- Sample surface

For improving the overall performance of the system, these factors had to be eliminated or minimised as much as possible. Surrounding the whole Kelvin capacitor with a Faradaic shield [10, 8] helps to reduce stray vibrations, magnetic and electrostatic coupling. The reference electrode was also surrounded with a driver shield [9, 14], which prevented current leakage. The probe tips were carefully polished flat using 1200-grade silicon carbide paper, cleaned with de-ionised water and acetone. Other factors, which can cause errors in measurements, are contamination of sample, oxidation or handling of surface, which can cause non-uniform work functions [38]. The use of a piezo-electric device reduces micro-phonic noise from the instrument [39].

CONCLUSIONS

The Scanning Kelvin Probe (SKP) Method is an indirect method to measure the electrochemical potential of a metal. Thus, in order to determine the potential of a given metal it is necessary to measure the Volta potential between it and an electrochemical reference electrode. Various designs of probes were developed to further improve the overall performance of the SKP system. Five novel probes were designed and tested with the SKP system probes were tested under certain parameters, corrosion potential measurements, height dependence and reproducibility. The tungsten wire probe was shown to be ‘best’ design for the SKP system.

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