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Citation: Review of Scientific Instruments **86**, 096101 (2015); doi: 10.1063/1.4930145
View online: http://dx.doi.org/10.1063/1.4930145
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REVIEW OF SCIENTIFIC INSTRUMENTS **86**, 096101 (2015)

Note: Design and fabrication of a simple versatile microelectrochemical cell and its accessories

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(Received 15 April 2015; accepted 24 August 2015; published online 8 September 2015)

A microelectrochemical cell housed in an optical microscope and custom-made accessories have been designed and fabricated, which allows performing spatially resolved corrosion measurements. The cell assembly was designed to directly integrate the reference electrode close to the capillary tip to avoid air bubbles. A hard disk along with an old optical microscope was re-engineered into a microgrinder, which made the vertical grinding of glass capillary tips very easy. A stepper motor was customized into a microsyringe pump to dispense a controlled volume of electrolyte through the capillary. A force sensitive resistor was used to achieve constant wetting area. The functionality of the developed instrument is demonstrated by studying μ-electrochemical behavior of worn surface on AA2014-T6 alloy. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4930145]

Novel experimental setups have been found in the recent years to study the electrochemistry and corrosion behavior of pure metals and alloys.[1–3] The need for fundamental understanding of corrosion at the microscale has led to development of new setups, experimentation, and analysis.[4,5] In the mid 1990 s, microelectrochemical cell was proposed for local corrosion studies.[6,7] Before the advent of microelectrochemical cell, the researchers performed local corrosion studies by masking technique using photoresist.[8] Though microelectrochemical cell is now a nearly 20-year-old technique, still commercialization of the equipment and the testing is not pervasive. The equipment is often custom-made by research groups, and hence many versions exist. Global corrosion studies are standard in testing, but the outreach to conduct the corrosion tests locally is still limited mainly due to technical challenges and number of accessories required. Testing of materials in spatially resolved manner is very much necessary due to heterogeneities in microstructures, different joints like welded samples, etc. Following are the list of individual components often required to build microelectrochemical cell.

- High resolution potentiostat capable of recording low current values as the area analyzed is small (μm^2).[9]
- Glass capillary puller to neck down (drawing) the capillaries to a tip diameter of few micrometers (100-500 μm).[10]
- Microgrinder to produce flat glass capillary tips of specific diameter.[10]
- Syringe pump to dispense electrolyte in controlled volumes to the cell.[9]
- Force sensor to sense and control the load applied when the capillary tip contacts the sample surface. This load has to be kept constant in order to have reproducible wetted area.[9]
- Acrylic cell which can house the reference electrode and counter electrode.[11]
- Video microscope to visualize the touching of the capillary tip onto the surface.[6]
- Optical microscope, if the analysis involves locating a specific grain or a phase in a material to conduct the corrosion test at the specific spot.[12]
- XYZ stage to position the working electrode.[6]

Typically, the cell mounted on the optical microscopes has reference electrodes located outside the cell.[9] Mardare[13] had placed reference electrode built inside the capillary without using the optical microscope. In this note, new cell design has been proposed to mount the cell in the turret of the microscope combined with the integration of microreference electrode close to the capillary tip to avoid air bubbles. Indigenously developed accessories like the syringe pump and microgrinder (using a hard disk and an old optical microscope) were fabricated. A simple force sensor has also been used. These precise accessories are tailor made for the microelectrochemical cell.

Glass microcapillaries were prepared by manually drawing borosilicate glass tubes of 3 mm outer diameter and 2 mm inner diameter into a very fine tip using a gas burner. The as-pulled capillary is shown in Fig. 1(a). The capillaries were drawn straight which ensures that the position of the tip coincides with the spot as identified through the optical microscope.

A flat capillary tip is extremely important for applying silicone rubber and to avoid any electrolyte leakage (confined droplet). A typical ground flat tip is shown in Fig. 1(b) and with silicone rubber sealing in Fig. 1(c). The flat capillary tip is achieved by using a vibration free grinding wheel to successfully grind/polish the glass capillary without any breakage. For this, a hard disk was modified into an automated microgrinder. Fig. 1(d) shows the photograph of the in-house built microgrinder. This uses a 30 A electric speed control (ESC) along with Arduino Uno microcontroller board based on the ATmega328. The rotation speed can be controlled utilizing a program. A silicon carbide grinding paper of 3000 grit size was used as the abrasive medium to grind the glass capillary to obtain flat tips. Also, wet grinding using water as a lubricant

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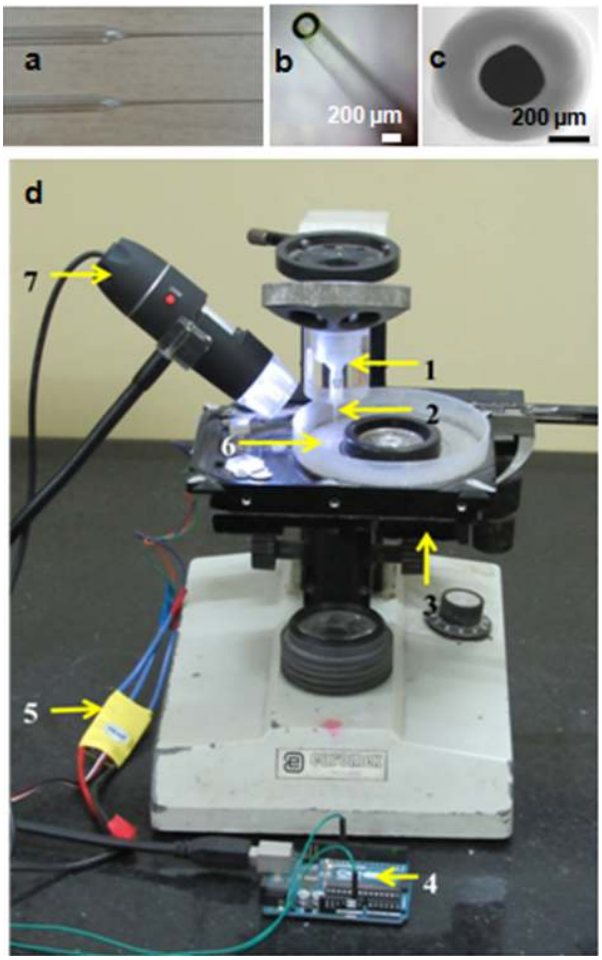

FIG. 1. (a) Pulled glass capillaries. (b) Optical image of ground glass capillary tip. (c) SEM micrograph of the capillary tip with silicone rubber. (d) Hard disk modified microgrinder. 1—Capillary holder, 2—glass capillary, 3—XYZ stage, 4—Arduino microcontroller, 5—electric speed control (ESC), 6—reservoir/boundary, and 7—video microscope.

was made possible by modifying the hard disk with a reservoir which avoids seeping of water into the motor and its control systems.

The capillary holder is fitted to the turret of an old optical microscope to which the glass capillary was fixed and the hard disk modified microgrinder was mounted on the xyz stage of the microscope. Vertical grinding without any tilt in the position of capillary was achieved easily. The grinding process was observed through a video microscope.

To dispense electrolyte through the capillary onto the specimen surface, a stepper motor was used to fabricate a syringe pump along with Arduino microcontroller interface as shown in Fig. 2. It has a fixed and movable acrylic plate between which the syringe is placed to dispense the electrolyte into the acrylic block and to the capillary.

The rotational speed of the stepper motor and the volume of the syringe control the flow rate. A potentiometer is used to vary the speed of the motor. A flow rate of 3 μl/min was achieved by using a 50 μl syringe and slow rotation of the stepper motor. It can hold 2 syringes of different volumes.

In order to obtain a constant wetting area on the specimen, a square shaped force sensitive resistor (force sensor) was

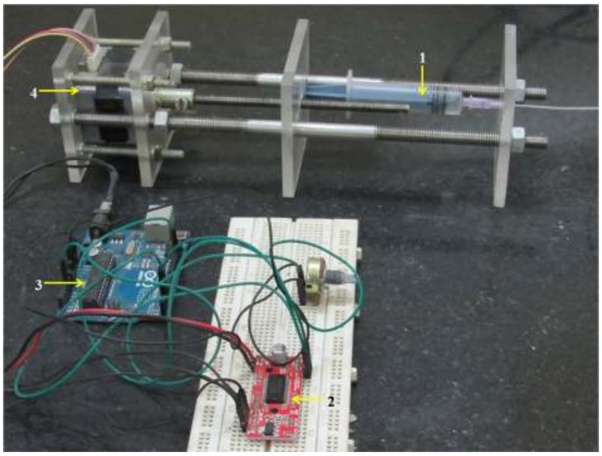

FIG. 2. Stepper motor controlled syringe pump. 1—Syringe, 2—stepper motor driver, 3—Arduino microcontroller, and 4—stepper motor.

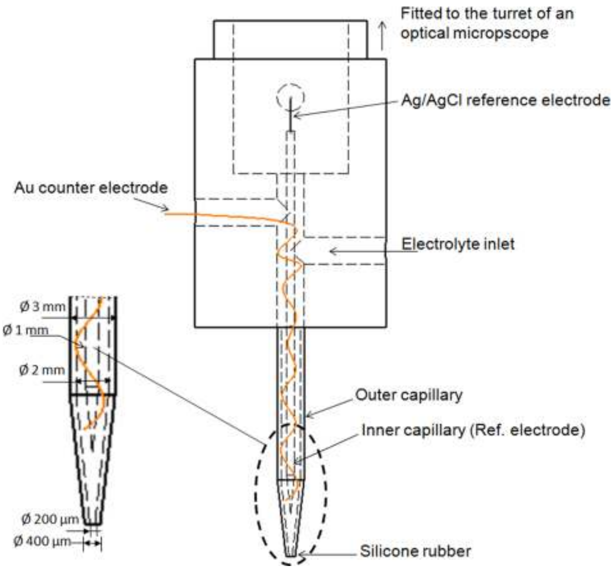

FIG. 3. Schematic of the microelectrochemical cell.

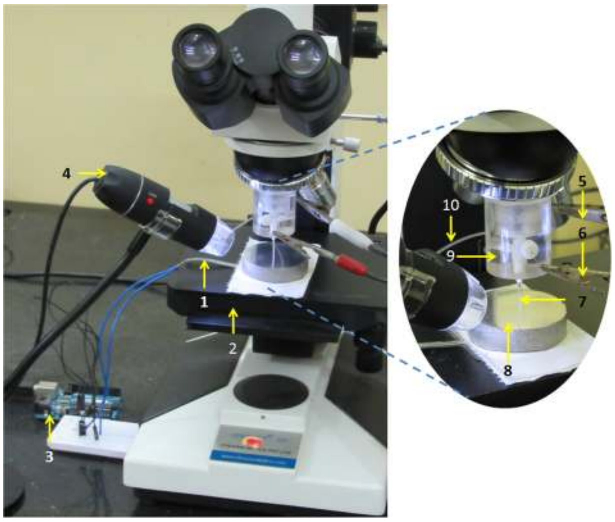

FIG. 4. Microelectrochemical cell mounted on the turret of optical microscope. 1—Force sensor, 2—XYZ stage, 3—Arduino controller, 4—video microscope, 5—reference electrode, 6—counter electrode, 7—glass capillary, 8—working electrode, 9—cell, and 10—electrolyte inlet.

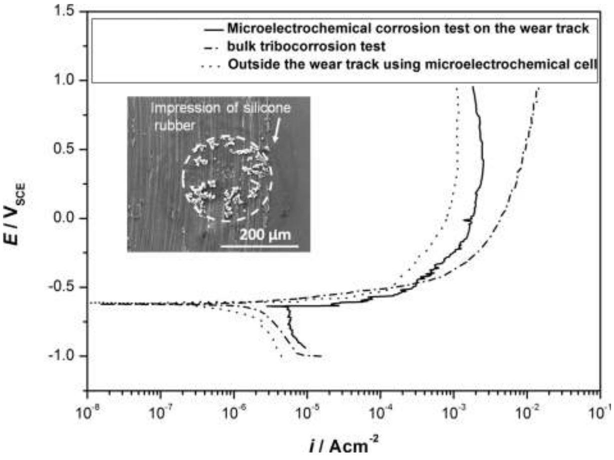

FIG. 5. Potentiodynamic polarization curves of bulk and microscale on AA2014–T6 in 0.1M NaCl solution. Inset: SEM micrograph showing corrosion tested area on the wear track using microelectrochemical cell.

used to control and apply constant contact pressure of the capillary onto the sample surface. Application of force leads to change in the resistance, which can be observed using Arduino microcontroller interface.

The force sensor was placed beneath the sample with a thin insulation separating them. As the specimen surface touches the capillary tip, increase in load leads to change in resistance. This value is maintained constant for all the measurements carried out at different spots. For calibration, the resistance values were recorded for every specimen tested with different dimensions and weights ensuring constant wetting area.

The cell was designed in such a way to fit into the turret of an optical microscope as shown in Figs. 3 and 4. Channels were made to connect electrolyte inlet, counter electrode, and reference electrode.

Here, for the first time, we have successfully integrated the reference electrode within the tip which is used with a microscope. Au wire of 0.25 mm diameter was used as counter electrode and Ag/AgCl reference electrode was prepared as reported by Hassel *et al.*[10]

The versatility of the developed instrument is demonstrated by studying μ-electrochemical behavior of worn surface on AA2014-T6 alloy. The wear track was formed using pin on disk modified tribocorrosion experimental setup using alumina ball of diameter 6 mm with a load of 2.5 N at 10 rpm. Fig. 5 shows the SEM micrograph (inset) of AA2014-T6 specimen corrosion tested in 0.1M NaCl solution using microelectrochemical cell on a wear track. The polarization studies were carried out using high resolution Gamry potentiostat (Reference 600). The curves compare the overall corrosion behavior of 1 cm^2 area with local corrosion of 200 μm diameter spot within and outside the wear track.

The curves reveal that the corrosion rate on the worn surface is higher than bulk due to mechanical effects. The corrosion rate of non-worn area is lesser than the worn area. The tests were repeated at least three times to check reproducibility of the data.

It is noteworthy to conclude that the fabricated cell has the potential to perform spatially resolved corrosion measurements at spots of interest on the metal surface. Resolution of the potentiostat is the main limitation with the microelectrochemical cell. Lower capillary diameters (tens of μm in diameter) and conductivity of the electrolyte will increase the ohmic resistance leading to potential drop. Electrochemical studies of intermetallic compounds in aluminium alloys are planned as a future work using glass capillary with smaller tip diameters.

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