The electrode potential of freshly generated aluminium surfaces in lubricating oil

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This paper describes the electrode potential of freshly generated aluminium surfaces measured using the guillotined electrode whilst it is submerged under lubricating oil. An initially low value of the bared metal surface is followed by a slow rise towards the steady state as repassivation proceeds. The presence of lauric acid, a surfactant, in the oil raises the potential of the initially bared surface, demonstrating its direct cathodic activity in the electrochemical reaction, an effect which decreases as repassivation progresses.

**KEY WORDS:** aluminium surface, electrode potential, guillotined electrode, lubricant, surfactant

1. Introduction

In strip rolling of aluminium, the friction between the roll and the strip influences the surface quality of the finished product, and the production efficiency. Mechanical modelling and analysis of the transfer film on the roll surface indicates that cold metal rolling is in the boundary lubrication regime. In this condition, hydrodynamic entraining of the oil, and asperity contact between the roll and the strip exist at the same time [1]. When the aluminium strip is elongated through the bite a virgin aluminium surface is created by rupture of the surface oxide film. The reaction between the denuded aluminium surface and the additives in the lubricant or other species in the local environment is an important issue in the understanding of the mechanism of boundary lubrication between the roll and the strip.

Various methods have been used to investigate the tribochemical interaction between the lubricant additives and the materials of the sliding surfaces in several tribology systems. To analyse the transfer film generated, and the changes of the chemical compositions of the surfaces, X-ray absorption [2,3], X-ray photoelectron spectroscopy [4], Auger electron spectroscopy [5,6] and Raman spectroscopy [7] have been used. With the exception of Raman spectroscopy, these \textit{ex situ} techniques give potential information about the state of the surface, but only after removal, washing and inserting into a vacuum chamber. The electrical contact resistance between the roll and the strip has also been measured [8,9], and this was done \textit{in situ}. However, it is difficult to use this type of information to elucidate mechanisms of the boundary lubrication involved.

One possible method for this, as shown below, is the use of the guillotined electrode [10–13], a technique developed for analysis of freshly generated surface in aqueous solutions. The guillotined electrode technique requires a sharp unreactive blade to be driven rapidly through a specimen of the metal under submersion, and the electrode potential of the metal to be measured simultaneously against an appropriate reference electrode. In previous experiments [10–13], the cutting edge was made of boron nitride and employed a spring-loaded guillotine assembly to cut the metal at speeds of around 1–2 m s\textsuperscript{-1}. Apart from a saturated calomel reference electrode (SCE), the equipment was also fitted with a platinum counter electrode so that the test metal could be held under electrochemical control, either potentiostatically or galvanostatically [11,14]. In this way the electrode potential could be monitored \textit{in situ} as a function of time through the guillotining process and afterwards. The effects of the environment could be interpreted unambiguously, as for example, the role of chromate on the potential of the repassivating metal [12]. Experiments were also carried out in water of low conductivity, such as tap-water and even distilled water [13].

In this paper, we present the preliminary data describing the electrode potential of the bared metal surface, obtained by guillotining aluminium whilst it is submerged in a lubricant system, and thereby demonstrate a quantitative role of a surfactant additive, in this case lauric acid (dodecanoic acid), incorporated into the oil.

2. Experimental method

Figure 1 shows the guillotined electrode cell and assembly. A rectangular cell constructed of
Polytetrafluoroethylene (PTFE) was fixed to a solid steel base which was bolted to the bench. The test material was pure aluminium (Johnson-Matthey, 99.999\%\%) in the form of wire of diameter 1 mm. This was threaded through an axial hole drilled into a 6-mm diameter rod made of PTFE, with a thin film of epoxy resin covering the metal surface. A steel blade with the edge sharpened as a cutting surface was attached to the aluminium carriage, which was mounted so as to be able to travel on four parallel steel rods positioned between the two holding frames. At first the carriage and springs were pushed to the lower, left-hand end of the travel, and held there with a catch. Release of the catch allowed the blade to be spring-driven upwards, through the end of the sample which had been positioned so that the end protruded through the block. Full details of the method have been given by Burstein and Cinderey [10]. The difference in present design is the fact that the blade here is driven upwards, so that when the guillotining action is complete, the blade has cleared the newly cut surface completely. This allowed easy access of a Luggin capillary probe for logging the potential. The Luggin capillary probe was connected to a tube filled with the lubricating oil from the cell for about 10 cm. The remaining length of tube remote from the cell, was filled with an aqueous solution containing an agar gel (made from 3 g agar and 30 g KCl in 100 cm$^3$ water) and it was into this that the reference electrode was placed. The reference was an aqueous SCE. The liquid junction between the oil and the aqueous gel solution was not estimated, and the potentials given below are therefore relative to the aqueous SCE scale. The potential between the guillotined electrode and the SCE reference electrode were monitored using a high-impedance electrometer (Keithley model 6571) which fed directly into a data-acquisition card (PCI-9114A, from ADLINK Technology Inc., 32 bit) mounted into a personal computer. Data were logged at a higher rate (between 20 and 100 kHz) during early stages of repassivation and at lower rate (between 1 and 1000 Hz) during later stages.

The metal was guillotined in Somentor grade 32 lubricating oil supplied by ExxonMobil Ltd., a mixture of saturated hydrocarbons. Because of the extremely low conductivity ($\sigma$) of the oil ($\sigma = 13.3$ IS cm$^{-1}$), a conductivity improver, Octastat 3000 (Octel Corp., Manchester, UK) was added to a concentration of

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Figure 1. Upper: Schematic diagram of the guillotined electrode assembly for experiments with lubricants. (a) working electrode (aluminium wire) sleeved in PTFE; (b) PVC tube with agar gel for the reference electrode; (c) steel blade; (d) carriage made of aluminium alloy; (e) spring; (f) upward direction of the guillotine when the sample is being cut; (g) steel framework; (h) test lubricant in PTFE cell; (i) PTFE block; (j) PTFE block equipped with sample feed. The diagram shows the guillotine in its activated position, with the sharp edge of the blade approaching the protruding aluminium wire. Lower: The guillotine blade showing the cutting edge and the relative position of sample to be cut.