Effect of Sulfate Concentration on Surface Roughness on Anodic Dissolution of Inconel 718 and SS304 in Sodium Nitrate Solution

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Abstract - The electrolyte plays a crucial role in the stability of electrochemical machining processes, however, over time the composition can change from the initial. Sodium sulfate accumulates in ECM electrolytes as a by-product from chromium VI reduction but it is difficult to selectively remove from the electrolyte. It is important to understand how these changes may affect machining. This paper investigates the effect a changing concentration of sodium sulfate in a sodium nitrate electrolyte has on the surface roughness after potential pulses are applied in a laboratory set up on SS304 and Inconel 718.

Keywords: Electrochemical Machining; Sodium Nitrate

I. INTRODUCTION

Electrochemical machining (ECM) is a non-conventional machining technique which utilises the anodic dissolution to remove material. Material is removed in the inverse shape of the tool shape (1).

ECM does not impart typical machining stresses into the material as it is a contactless, almost heat-free method. As such, ECM can be used to machine brittle materials. Machining success is also not dependent on the material hardness, so very hard materials, such as super alloys, can be easily machined (1). High surface finishes can be achieved but is dependent on a number of machining parameters (2).

The quality of the machined surface after ECM can be affected by flow conditions in the inter-electrode gap (3), the small space between the tool and the work piece, the voltage(1), the pulse length and duty cycle (4) and the electrolyte composition.

In ECM, a small gap, on the order of microns, is maintained between the tool, AKA the cathode and the work piece AKA the anode (5). Electrolyte is flushed through this small gap at a high flow rate to remove the reaction products. These reaction products, if not removed, will cause problematic machining, from causing sparks between the two electrodes to choking the electrolyte flow due to a build-up of gas in the gap. In some cases, electrolyte flow paths can be observed on the finished product if insufficient flushing is not maintained (3).

The voltage is a crucial factor for the success of ECM; the voltage is the parameter that provides the work for the material removal. For each ECM system there is a minimum voltage that must be reached for anodic dissolution to occur. A higher voltage, to a certain point, will increase the machining rate (6). Many researchers have however observed that an increased voltage reduces machining precision (6) but also that an increased voltage produces a higher quality surface finish (7). A compromise must be made for the voltage used to balance the precision, machining rate and the surface finish.

The applied pulse length and duty cycle may also affect both the machining accuracy and the surface finish achievable (4). Using a short voltage pulse restricts the areas on the work piece which are sufficiently charged for anodic dissolution to occur (8). Reactions are confined to areas on the work piece which are in close proximity to the tool. This can be utilised along with the electrolyte choice to discriminate between peaks and troughs in the work piece surface, resulting in a polished finish.

The electrolyte composition can also affect the machining quality. Active electrolytes contain aggressive anions such as chloride and do not allow passivation of the work piece surface, but low potentials, when using these electrolytes, encourage pitting. (9) This results in a poor surface finish. Passive electrolytes, such as sodium nitrate, create a protective layer on the work piece surface. This aids machining precision and pitting is less likely. Typically, an ECM surface in a passive electrolyte is smoother than that produced by an active electrolyte.

This paper will investigate the effect of sulfate concentration in a sodium nitrate electrolyte on the surface roughness of stainless steel 304 (SS304) and Inconel 718. Sulfate is a by-product of some chromium VI reduction techniques. It is difficult to selectively remove sulfate from the electrolyte, so it is important to understand how its presence at varying concentrations can affect the surface finish.

II. METHODOLOGY

A number of electrolytes were made with varying ratios of sodium nitrate and sodium sulfate. Each electrolyte was adjusted to pH 8.5 and a conductivity of 85 mS cm^{-1}. See Table 1 for the variations that were made.

A 1 mm diameter nickel wire was insulated with heat shrink wrap so only the end of the wire was exposed. The end of the wire was polished to a mirror finish using a series of progressively finer sandpapers.

Chronoamperometry experiments were conducted using an IviumStat potentiostat. Voltage pulses of 7.5 ms at 10 V were applied with 32.5 ms pauses between each pulse. The pulses were applied for a 15000 cycles of paired pulses and pauses which totalled 10 minutes. An initial gap of 100 µm was established between the end of the nickel wire tool and the work piece. The work piece was either a SS304 or Inconel 718 disc. The electrolyte was stirred by a small magnetic stirrer bar and all experiments were conducted at room temperature. The tool was stationary throughout.

All chemicals were ACS reagent grade chemicals from Sigma Aldrich and the purified water was from an ELGA PURELAB Option-Q water purifier.

III. RESULTS AND DISCUSSION

ECM is a sensitive technique but when all parameters are closely controlled machining is consistent and predictable. One of the most critical variables in the setup is the electrolyte. During machining metal ions are dissolved into the electrolyte, most of these are precipitated as metal hydroxides and removed by filtration. However, chromium VI is highly soluble and remains in the electrolyte. Chromium VI is a known carcinogen and so efforts are made to reduce and remove this from the electrolyte. One of the most efficient reduction methods generates sodium sulfate which accumulates over time due to its high solubility. It is unknown how this slow accumulation affects the quality of the surface finish during machining.

Figure 1 shows the typical current response during chronoamperometry for a limited number of voltage pulses. The current rises rapidly as the surface is charged. There is a small negative current observed when the potential is returned to 0 V, this again is the charging current. It is during the pulse that material is removed. The period of time where no current is flowing allows the machining products to be removed from the machining gap. The pulse also helps to confine machining to areas close to the tool electrode.

Figure 2 shows the surface roughness measurements for SS304 in the range of nitrate-sulfate electrolytes used. The lowest surface roughness appears with a pure sodium sulfate electrolyte, closely followed by a pure sodium nitrate electrolyte. The highest surface roughness was observed with a 50:50 nitrate-sulfate electrolyte.

There is an approximate negative parabolic trend with respect to the surface roughness as a result of increasing sulfate/decreasing nitrate concentration. Both nitrate and sulfate electrolytes are known to be passive electrolytes. It is possible nitrate has a higher affinity for one of the alloy components and sulfate for another. As the concentrations of each of the ions reach a similar level, there are more surface sites on the alloy that are strongly passivated compared to the number occupied in a predominately nitrate or sulfate electrolyte. Pitting, or uneven removal of the passive layer, is more likely to occur in this situation; as such a rougher surface finish would result.

Figure 3 shows the surface roughness measurements for Inconel 718 in the range of nitrate-sulfate electrolytes used. This shows a clearer trend here in that, in general, the surface roughness increases with sulfate concentration. This indicates that a higher sulfate concentration facilitates pitting corrosion, increasing the surface roughness.

Overall, the surface roughness is lower for SS304 compared to Inconel 718 in all cases. This is to be expected as the chromium content in SS304 is lower than in Inconel 718 which results in a less protective oxide layer. This layer is more easily removed, requiring a lower applied potential to break through to fresh material. This reduces the likelihood of a pitting mechanism occurring during machining; hence the surface roughness is lower. This may also be in part due to the metallic grain structure of the material.

The variation in surface roughness is wider for Inconel 718, varying by approximately 3 µm versus only 1.4 µm for SS304. It is more important to control the sulfate concentration for Inconel 718 than it is for SS304 in order to minimise the surface roughness.

These results are only indicative of the overall trend not the expected final results achievable in an ECM environment. The electrolyte was not sufficiently flushed though the machining gap due to available resources. This will have resulted in a build-up of machining products in the gap, potentially causing sparks or lower machining rates than would usually be expected.

IV. CONCLUSION

It is important to understand how a changing ratio of sodium nitrate to sodium sulfate in the electrolyte can affect ECM results in terms of the surface roughness due to the accumulation of sulfate from the chemical reduction of chromium VI. This paper showed that either a pure sodium nitrate or sodium sulfate electrolyte resulted in the lowest recorded surface roughness with SS304 but a mix of the two salts created a higher surface roughness. With Inconel 718, the lowest surface roughness was produced with pure sodium nitrate and an increase in sodium sulfate increased the surface roughness.

V.   REFERENCES

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Table 1 Ratio of NaNO3 and Na2SO4 for electrolyte composition

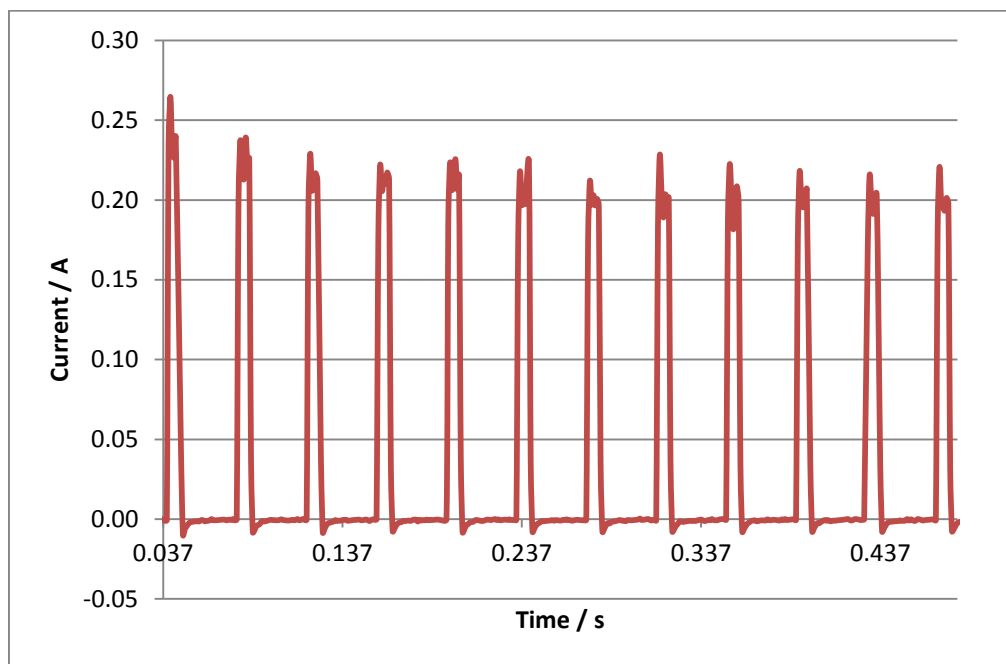| Percentage of Sodium Nitrate	Percentage of Sodium Sulfate
100	0
90	10
70	30
50	50
30	70
10	90
0	100

Figure 1 Typical chronoamperometry result for voltage pulses applied for 7.5 ms, only a few pulses are shown here
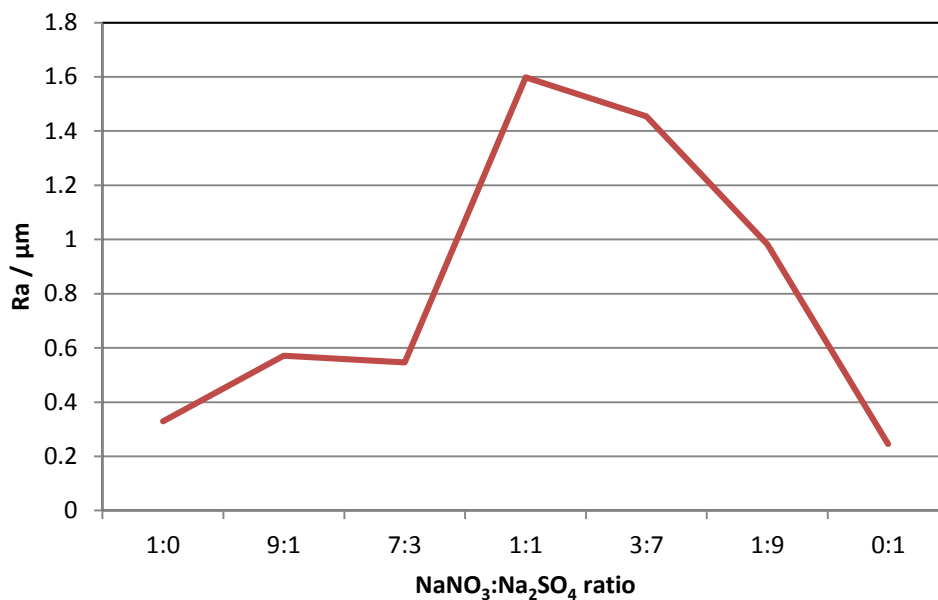
Figure 2 Surface roughness measurements for SS304 at various nitrate:sulfate ratios
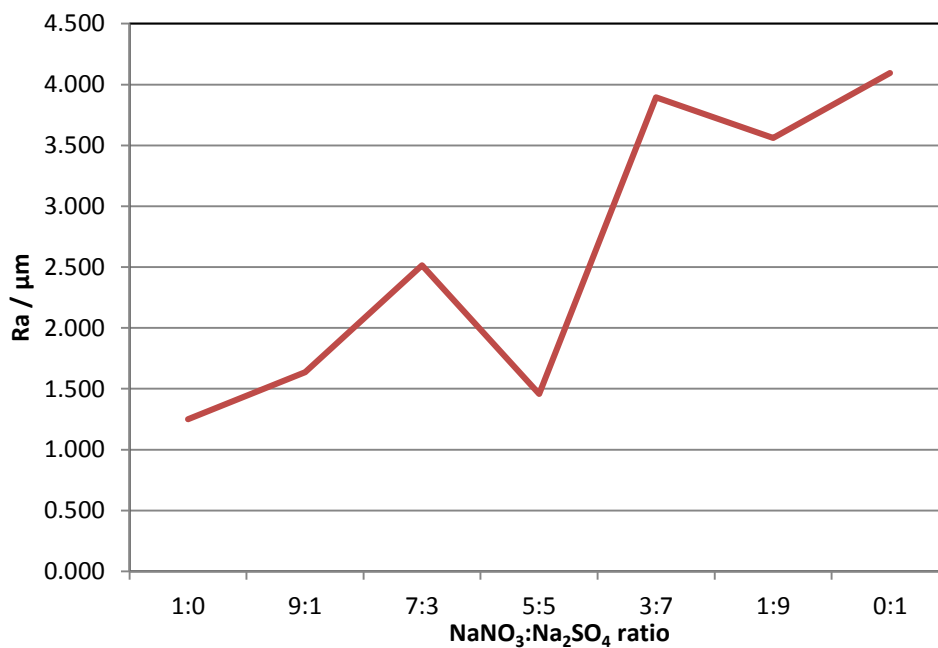

Figure 3 surface roughness measurements for Inconel 718 at various nitrate:sulfate ratios