Lawrence Berkeley National Laboratory
Recent Work

Title
ELECTROCHEMICAL MACHINING OF CEMENTED TITANIUM CARBIDE

Permalink
https://escholarship.org/uc/item/0mh584v6

Authors
Coughanowr, C.A.
Muller, R.H.
Tobias, C.W.

Publication Date
1982-08-01
ELECTROCHEMICAL MACHINING OF CEMENTED TITANIUM CARBIDE

Corinne A. Coughanowr*, Rolf H. Muller, and Charles W. Tobias

(*M.S. Thesis)

August 1982

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
ELECTROCHEMICAL MACHINING OF CEMENTED TITANIUM CARBIDE

Corinne A. Coughanowr
(M.S. Thesis)

with Rolf H. Muller and Charles W. Tobias

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

August 1982

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
To My Parents
TABLE OF CONTENTS

Abstract

I. Introduction. .............................................. 1
   A. The ECM Process ..................................... 1
   B. Scope of the Present Work ............................ 3

II. Detailed Description of ECM ........................... 5
   A. Characteristics of ECM Operation .................... 5
   B. Electrochemical Relations ............................ 8
      1. Valence of Dissolution ......................... 8
      2. Ohmic Drop and Overvoltage ...................... 10
      3. Interelectrode Gap .............................. 12
      4. Conductivity of the Electrolyte .................. 14
   C. Electrode Reactions ................................. 15
      1. Anodic Reactions .................................. 15
      2. Cathodic Reactions ............................... 17

III. Materials ........................................... 18
   A. Anode Materials .................................... 18
   B. Toolpieces .......................................... 20
   C. Electrolyte ......................................... 30

IV. Experimental Equipment and Procedure ................ 23
   A. ECM Equipment ...................................... 23
   B. ECM Run Procedure ................................. 26
      1. Before ECM Run .................................. 26
      2. During ECM Run .................................. 27
      3. After ECM Run .................................... 27
   C. Estimate of Experimental Error ..................... 28
   D. Surface Analysis Instruments ....................... 38

V. Results ............................................... 33
   A. ECM Behavior ........................................ 33
      1. Titanium Carbide ................................ 33
         a. Valence of Dissolution ....................... 33
         b. Current-Voltage Relationship ................. 35
         c. Interelectrode Gap Correlations .............. 40
ELECTROCHEMICAL MACHINING OF CEMENTED TITANIUM CARBIDE

Corinne A. Coughanowr with Rolf H. Muller and Charles W. Tobias

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and Department of Chemical Engineering,
University of California, Berkeley, California 94720

ABSTRACT

The electrochemical machining (ECM) of a cemented titanium carbide/10% nickel composite has been investigated and compared to the ECM of the pure components, TiC and Ni. All three materials were machined in 2M KNO₃ electrolyte, under current densities ranging from 17 to 100 A/cm².

The ECM behavior of the TiC/Ni composite was found to be intermediate to that of its components. The apparent valences of dissolution for all three materials were independent of current density in the range studied: 2.8 eq/gmol for Ni, and 6.6 and 6.5 eq/gmol for TiC and TiC/Ni, respectively. Linear cell voltage versus current density relationships were obtained for all three materials.

Surface analysis of the TiC/Ni composite showed preferential dissolution of the TiC phase over the nickel phase for the entire range of operating conditions investigated. A polishing regime could not be identified for cemented TiC/Ni.
I. Introduction

A. The ECM Process

Electrochemical machining (ECM) is a process of metal removal via high-rate anodic dissolution. The material to be shaped, called the workpiece, is made the anode, and a metal toolpiece is chosen for the cathode, with a shape complementary to that which is to be obtained in the workpiece. The workpiece is held stationary, and the toolpiece is mounted opposite and advanced towards it at a steady rate, while an electrolyte solution is pumped between the electrodes at a high rate. The electrolyte not only maintains electrical contact between the electrodes, which never touch, it also serves to carry away the dissolution products and to remove the heat evolved.

While the ECM process is a capital-intensive one, compared to traditional, mechanical methods of machining, it has several features which make it commercially attractive for certain applications. Since the metal removal in ECM is effected by electrolytic dissolution, the main requirement for the machinability of a material is that it be an electronic conductor; the ECM of the material will be affected by its electrochemical behavior and not by its hardness. Thus cutting time and toolpiece wear for the machining of very hard materials are much reduced in this process.

Another significant feature of ECM is that the workpiece can be shaped to the desired profile, simply by choosing the appropriate geometry for the toolpiece. In many instances, ECM can be used to produce shapes that are difficult or impossible to obtain using common rotating tools. Finally, the fact that the electrodes never touch means that
the surface of the workpiece is left stress-free afterwards, unlike with conventional machining methods.

Electrochemical machining is a recently developed method in the history of shaping of metals. The first practical applications were investigated in the 1950's by the Battelle Memorial Institute, which developed the electrochemical grinding of carbide-tipped tools and the shaping of gas-turbine blades. Since then, numerous patents have been issued on the subject of ECM, covering such aspects as toolpiece design, equipment construction, choice of electrolyte for the machining of specific metals and various applications of the technique.

Among the types of ECM performed commercially, two of the most important are drilling and shaping; other applications include turning, trepanning, cutting, milling, and finishing. The aerospace industry uses ECM to shape blades for gas-turbine engines, and electrochemical drilling to produce cooling holes in the blades. Shaped apertures are cut in piston engine sleeve valves by electrochemical trepanning. Electrochemical honing and deburring are used in the automotive industry for finishing metal parts.

The extended application of ECM in industry has been limited not only by the high capital investment required, but also by the empirical nature of the technique. Toolpiece design as yet involves trial-and-error testing, and the choice of operating conditions (applied voltage, toolpiece advancement rate, electrolyte flow rate) and electrolyte for the machining of a particular metal is based more on empirical knowledge than on theoretical prediction. In the interest of improving the predictability of this process, many researchers have been investigating...
different aspects of ECM. A fairly recent and thorough review of the field has been presented by J. Bannard, and several books covering the principles and applications of ECM have been published.  

B. Scope of the Present Work

In this research, the ECM behavior of three materials was investigated: titanium carbide, nickel, and a composite of titanium carbide and nickel binder. Due to its qualities of high temperature stability, low density, high hardness, and good oxidation resistance, titanium carbide is used in industry to make parts which require superior wear resistance, such as nozzles, seal rings and bearings, valve parts, and tool tips.  

As titanium carbide in the pure form is very brittle, a binder is usually added to impart qualities of toughness and impact resistance. Nickel is almost always the metal chosen in industry as the binder; the amount of nickel in the cemented TiC/Ni composite ranges from 5 to 30%.  

A cemented TiC/Ni composite with a nominal composition of 90% TiC and 10% Ni was chosen for this study, along with samples of pure TiC and Ni (nickel 200). After investigating the ECM behavior of each material, the anode surfaces after machining were analyzed for the presence of an oxide layer formed during ECM. To detect preferential dissolution of one phase over the other in the TiC/Ni composite, post-machining surface compositions were determined over the range of operating conditions used. The final objective was to investigate the possibility of predicting not only the ECM behavior, but also the optimum ECM conditions for the composite material, based on the behavior of the pure components.
The electrolyte employed in this investigation was 2 M KNO₃, and a cylindrical toolpiece geometry was selected; these choices follow previous work in this laboratory on titanium carbide.⁶,⁷
II. Detailed Description of ECM

A. Characteristics of ECM Operation

The independent variables that are set when operating ECM equipment are the voltage applied across the electrodes, the advancement rate of the toolpiece, and the flow rate of the electrolyte. The dependent variables that are measured include the current, the pressure and temperature of the electrolyte, and the mass loss of the workpiece. An important parameter that is determined after machining is the interelectrode gap.

Relative to other electrolytic processes, the values for the applied voltage employed in ECM are high, on the order of 15 volts. High current densities, generally ranging from 50 to 150 A/cm², are achieved by use of high voltages, close electrode spacings and high flow rates. Toolpiece feed rates are set around 1 mm/min; this is relatively slow compared to the machining rates for the softer metals using conventional methods, but for hard materials the ECM rates compare much more favorably.

It is desirable to keep the interelectrode gap in ECM as small as possible, in order to minimize the ohmic losses and to obtain in the anode a replica of the cathode geometry which is as accurate as possible. In electrochemical drilling, for example, the hole made in the workpiece will always have a diameter larger than that of the toolpiece, due to stray current attack. The magnitude of the difference will depend on
the operating conditions used; a lower applied voltage and/or a higher toolpiece feed rate will result in a smaller interelectrode gap and a smaller hole diameter. In practice, the size of the interelectrode gap is on the order of 0.4 mm, and the magnitude of the diameter difference is on the order of 0.3 mm.

Before commencing to drill a hole by ECM, a starting gap is set between the electrodes. As the machining proceeds, the interelectrode gap adjusts according to the toolpiece feed rate and the applied voltage, until steady-state conditions are reached. In this case, the advancement rate of the cathode matches the mass removal rate at the anode, and the interelectrode gap maintains a constant value.

If the operating conditions are altered slightly, the system will adjust automatically, and the change will be reflected in the size of the gap. For instance, an increase in applied voltage will drive more current through the electrolyte, the mass removal rate at the anode will increase, and the gap will increase until the ohmic drop in the electrolyte and the surface overvoltages have risen to the level of the new applied voltage. The system reaches a new steady-state where the mass removal rate matches the feed rate, and the interelectrode gap has a new, larger, constant value.

For the case where the toolpiece feed rate is increased, the gap will decrease, diminishing the resistance through the electrolyte and raising the current flowing through the system. The metal removal rate will rise until it matches the new feed rate.

The most important characteristic of the electrolyte is its conductivity. Most ECM electrolytes have a concentration of 2 to 6
molar of one or more salts; conductivities are generally around 0.2 $\Omega^{-1}\text{cm}^{-1}$ at operating temperatures near ambient.

The electrolyte flow rate in ECM should be high for several reasons. Since the passage of high current densities results in significant Joule heating, the flow rate needs to be high enough to minimize the temperature rise of the electrolyte as it passes between the electrodes. It is also desirable to remove the reaction products quickly, because solute species would have a chance to reach the cathode where they could be reduced, while solid products could cause passivity and consequent oxygen evolution. The electrolyte is often chosen so that the metal ions generated by oxidation at the anode will react in solution to form an insoluble oxide or hydroxide. This precipitate can then be filtered out, and the electrolyte can be recirculated with minimum contamination.

The principal reaction at the cathode is hydrogen evolution. A high electrolyte flow rate is effective in carrying the gas bubbles out of the interelectrode gap, and preventing a blanket of gas from covering the cathode.\(^8\)

Applied electrolyte flow rates depend on the size of the component to be machined and can reach several hundred liters/min. The corresponding linear velocities through the gap range from 5 to 50 m/sec, and the flow is always in the turbulent range ($\text{Re} > 3,000$). The pressure drop across the tool-workpiece pair may reach high values, up to 500 psi.
B. Electrochemical Relations

1. Valence of Dissolution

For electrolytic dissolution of an element, Faraday's Law states:

\[ \Delta m = \frac{I \cdot t \cdot M}{F \cdot z \cdot CE} \quad (1) \]

where \( \Delta m \) = mass loss of element
I = current
\( t \) = time
\( F \) = Faraday's constant = 96,500 C/eq
\( M \) = molecular weight of element
\( z \) = valence of dissolution
\( CE \) = current efficiency of the dissolution reaction

By assuming a current efficiency of 100%, one can solve this equation for the apparent valence, \( z_{app} \):

\[ z_{app} = \frac{I \cdot t \cdot M}{F \cdot \Delta m} \quad (2) \]

The mass removal rate of the element, \( \dot{m} \), is obtained by another rearrangement of Faraday's Law:

\[ \dot{m} = \frac{\Delta m}{t} = \frac{I \cdot M}{F \cdot z_{app}} \quad (3) \]

For steady-state conditions where a cylindrically-shaped hole is being electrochemically drilled, the mass removal rate can be related to the toolpiece feed rate in the following way:

\[ \dot{m} = \frac{\Delta m}{t} = \left( \frac{\text{Vol}}{t} \right) \rho = \frac{h \cdot a \cdot \rho}{t} = Fr \cdot a \cdot \rho \quad (4) \]
where $\text{Vol}$ = volume loss of element
$\rho$ = density of element
$h$ = depth of hole
$a$ = cross-sectional area of hole
$Fr$ = toolpiece feed rate

Combining equations (3) and (4), one obtains a relation between $Fr$ and $z$:

$$Fr = \frac{I \, M}{F \, a \, \rho \, Z_{\text{app}}} = \frac{i \, M}{F \, \rho \, Z_{\text{app}}} \tag{5}$$

For a set of data at different operating conditions, equations (3) and (5) give two separate methods for determining $Z_{\text{app}}$: one based on mass loss and the other based on volume loss. Plotting $\dot{m}$ versus $I$ and $Fr$ versus $i$ should yield straight lines with the following slopes:

$$\text{slope (} \dot{m} \text{ vs. } I ) = \left( \frac{M}{F} \right) \frac{1}{Z_{\text{app}}} \tag{6}$$

$$\text{slope (} Fr \text{ vs. } i ) = \left( \frac{M}{F \, \rho} \right) \frac{1}{Z_{\text{app}}} \tag{7}$$

The ECM process is used to machine not only pure metals, but also metal compounds and alloys. For such materials the valence of dissolution will depend on the composition of the material. To determine $Z_{\text{app}}$ from Faraday's Law, one needs a value for the molecular weight. For a binary substance containing by weight $x\%$ of component $a$ and $y\%$ of component $b$, the weighted molecular weight, $\overline{M}$, will be:

$$\overline{M} = x \, M_a + y \, M_b \tag{8}$$
Faraday's Law then becomes:

\[ \Delta m = \frac{I}{F} \frac{M}{z_{\text{app}}} \]  \hspace{1cm} (9)

and \( z_{\text{app}} \) can be determined by plotting \( \dot{m} \) vs. \( I \) and \( F_\text{r} \) vs. \( i \), as described above.

In order to determine the actual valence of dissolution for a material, one must know the current efficiency of dissolution:

\[ CE = \frac{I_{\text{theoretical}}}{I_{\text{actual}}} \]  \hspace{1cm} (10)

For a specific metal dissolution reaction, \( I_{\text{actual}} \) will be greater than \( I_{\text{theoretical}} \) when other oxidation reactions are taking place concurrently at the anode. If the amount of current going into the side reactions can be assessed, values for CE and \( z \) (actual) can be calculated.

2. Ohmic Drop and Overvoltage

The ohmic drop through the electrolyte between the electrodes, \( V_{ir} \), can be calculated by means of Ohm's Law:

\[ V_{ir} = IR = \frac{I}{a} \frac{\rho' \ell}{k} = \frac{i \ell}{k} \]  \hspace{1cm} (11)

where \( R \) = resistance
\( \rho' \) = resistivity
\( \ell \) = interelectrode gap
\( k \) = electrolyte conductivity
\( a \) = electrode area
The ohmic drop, $V_{ir}$, is smaller than the voltage applied across the electrodes, $V$; the difference, $\eta$, is the sum of the thermodynamic equilibrium potential, $E_0$, and the overvoltages:

$$V - V_{ir} = \eta = E_0 + \eta_a + \eta_c + \eta_r$$  \hspace{1cm} (12)

Overvoltage, caused by irreversible processes at both electrodes, has several sources. Two major types of overvoltage are the activation overvoltage, $\eta_a$, and the concentration overvoltage, $\eta_c$. The former arises from slowness in the actual transfer of charge from ions in the solution to the electrode, and the latter is caused by a limitation in the rate of mass transfer of ions to the electrode surface. Typically, $\eta_a$ and $\eta_c$ are represented by the following equations:

$$\eta_a = \beta \ln\left(\frac{i}{i_0}\right)$$  \hspace{1cm} (13)

where $\beta$ = a constant

$$i_0 = \text{exchange current density}$$

and

$$\eta_c = \frac{RT}{nF} \ln\left(\frac{C_i}{C_b}\right)$$  \hspace{1cm} (14)

where $n = \text{electrochemical valence of the ion discharged}$

$C_i = \text{concentration of ions at interfaces}$

$C_b = \text{concentration of ions in bulk solution}$
A third type of overvoltage is caused by a resistive film, such as an oxide film, which may form on the anode surface. This resistance overvoltage, $n_r$, may vary with current density, or it may be independent of current density if the film is a non-ohmic one. In either case $n_r$ can attain large values, on the order of several volts, compared to which $n_a$ and $n_c$ may become insignificant.

3. Interelectrode Gap

The interelectrode gap in ECM, $\lambda$, is determined after machining, from the starting gap set between the electrodes, $SG$, the depth of the hole after ECM, $h$, and the toolpiece advancement, $\delta$:

$$\lambda = h + SG - \delta$$  \hspace{1cm} (15)

This relation is illustrated in Fig. 1.

Since the operating conditions affect the gap, which in turn influences the dimensions of the hole drilled in the workpiece, it would be useful to obtain an estimate of the gap size before machining rather than afterwards, so as to be able to choose optimum values of $V$ and $Fr$.

By solving equation (11) for $\lambda$ and equation (5) for $i$, and combining them, one obtains a linear relation between the gap and a group, $d.f. = (kV_{ir}/Fr)$, called the ECM driving force: 6

$$\lambda = \frac{k V_{ir}}{i} = k V_{ir} \left( \frac{M}{Fr F z \rho} \right)$$

$$= \left( \frac{M}{Fr F z \rho} \right) \left( \frac{k V_{ir}}{Fr} \right) = a(d.f.)$$  \hspace{1cm} (16)

where $a$ is a constant for the system and would typically have units of $cm^3/C$. 
Fig. 1. Schematic diagram of tool-workpiece pair in ECM, showing dimensions used to determine the interelectrode gap, $l$. 
Using equation (12), one can substitute in \((V - \eta)\) for \(V_{ir}\) in the ECM driving force; one then obtains \(\xi\) in terms of the independent operating variables, \(V\) and \(Fr\):

\[
\xi = \frac{M}{F z \rho} \frac{k (V - \eta)}{Fr}
\]  

(17)

This relation is useful for making a rough estimate of the gap that will occur at the particular values of \(k\), \(V\), and \(Fr\) selected for machining, if one has an estimate of the overvoltage or makes the assumption that \(\eta \approx 0\).

4. Conductivity of the Electrolyte

The electrolyte conductivity, \(k\), depends on the temperature and concentration of the solution. Due to Joule heating during machining, the temperature rises substantially as the electrolyte flows between the electrodes, and the conductivity rises correspondingly.

The temperature dependence of conductivity is given by:

\[
k = k_0 \exp \left[ b(t - t_0) \right]
\]  

(18)

where \(k_0 = \) electrolyte conductivity at a reference temperature

\(b = \) constant for the particular electrolyte

\(t = \) temperature of interest (°C)

\(t_0 = \) reference temperature (°C)

For the case of a 2 M KNO_3 solution, \(b = 0.025\). At a reference temperature of 20°C, the value of \(k_0\) for this electrolyte is 0.15 \(\Omega^{-1}\) cm\(^{-1}\).

Using data for potassium nitrate solutions at a temperature of 20°C, one can make a linear approximation of \(k_0\) as a function of the solution density at the reference temperature, \(\rho_{20}\):
Since the concentration of the electrolyte is not measured directly in this work, but is derived from the measured specific gravity of the solution, the following relation is used to obtain a value for \( \rho_{20} \), based on the measured specific gravity, \( S_{15}^t \), and initial temperature, \( t_i \), of the solution:

\[
\rho_{20} = \frac{(0.9982) S_{15}^t}{(1.0070) - (0.0004) t_i}
\]

Combining equations (17), (18), and (19) yields:

\[
k = \left\{ (0.906) \left[ \frac{(0.9982) S_{15}^t}{(1.0070) - (0.0004) t_i} \right] - (0.868) \right\} \\
\times \exp \left[ (0.025) (t_a - 20) \right]
\]

where \( t_a \) is the average of the electrolyte temperatures before and after machining and has been substituted in for \( t \) (Eq. 16).

C. Electrode Reactions

1. Anodic Reactions

The basis of ECM is the metal dissolution reaction at the anode. The half-reaction for the oxidation of a metal anode has the following form:

\[
M \rightarrow M^{+z} + ze^{-}
\]

In neutral or basic solution this is followed by a chemical reaction between metal and hydroxyl ions to form a metal hydroxide which is
usually insoluble:

\[ M^{+z} + z(\text{OH}^-) \rightarrow M(\text{OH})_z \]  

(23)

The valence of dissolution, \( z \), ranges between +1 and +4 for most metals used in this process. The valence observed will have a non-integral value in many cases. Where the metal being machined is dissolving to two valence states simultaneously, the apparent valence will have an intermediate value, which will depend on the relative amounts of material going to each state. In the machining of alloys the valence of dissolution is the molar average of the valences of the components.

The apparent valence of dissolution will differ from the actual valence when there are side reactions occurring at the anode along with the metal dissolution. The predominant side reaction is oxygen evolution:

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \text{ (acid electrolyte)} \]  

(24)

\[ 4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^- \text{ (neutral or basic)} \]  

(25)

Such a side reaction will reduce the current efficiency for metal dissolution. To determine the current efficiency, either the true valence of dissolution or the amount of oxygen evolved must be known.

Metal dissolution in ECM proceeds in the active or the transpassive state. Concurrent oxygen evolution sometimes occurs when there is a resistive film layer on the anode, which is common in transpassive dissolution. The nature of the resistive layer, the rate of oxygen evolution, and the current efficiency of metal dissolution can vary with current density, electrolyte composition, and electrolyte pH.
2. Cathodic Reactions

The principal half-reaction at the cathode is hydrogen evolution:

\[ 2H^+ + 2e^- \rightarrow H_2 \quad \text{(acid electrolyte)} \quad (26) \]

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(neutral or basic)} \quad (27) \]

The hydrogen gas evolved is swept away from the electrode by the fast-flowing electrolyte.

An alternative reaction at the cathode is the reduction of electrolyte anions, such as chlorate to chloride ion, or nitrate to nitrite ion.\(^\text{12}\) Extensive participation of these anions in the electrode processes may lead to degradation of the electrolyte, although the tendency for hydrogen blanketing at the cathode will be reduced.\(^\text{8}\)
III. Materials

A. Anode Materials

Titanium carbide, nickel, and a composite of titanium carbide and nickel binder were the three materials chosen in this study for electrochemical machining. The first two were obtained commercially; pure titanium carbide pieces were supplied by the Haselden Company, San Jose, California, and nickel samples were cut from a rod of nickel 200.

The titanium carbide/nickel composite was fabricated on site, since the commercially available products are not binary, but contain substantial amounts of other carbides, such as niobium carbide, tantalum carbide, and tungsten carbide. The TiC/Ni specimens were produced from a mixture of 90% TiC powder and 10% Ni powder (by weight), using standard techniques of ball-milling, cold-pressing, and sintering (see Appendix I for details). The finished product turned out to contain tungsten carbide and cobalt as contaminants from the ball mill, which had a WC/Co lining and WC/Co balls. The amount of WC present in the composite was less than 4 mole%.

The compositions and selected physical properties of the three anode materials are shown in Table 1. The porosity of the fabricated TiC/Ni is about 11%, essentially the same as that of the commercially obtained TiC. The observed values for density, \( \rho_{\text{obs}} \), were determined from mass and volume measurements of the anode specimens, and porosities were obtained using the following equation:

\[
\text{porosity} = 1 - \frac{\rho_{\text{lit.}} - \rho_{\text{obs.}}}{\rho_{\text{lit.}}} \tag{28}
\]

where \( \rho_{\text{lit.}} \) is the density of the pore-free material reported in the literature.
<table>
<thead>
<tr>
<th>Material</th>
<th>Density obs.</th>
<th>Density lit.</th>
<th>Porosity</th>
<th>Molecular Weight</th>
<th>Composition (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>4.4</td>
<td>4.93</td>
<td>10.75%</td>
<td>59.911</td>
<td>Ti: 80%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C: 19.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe,Si,Ca,Na,O,N,H: each ≤ 0.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Ref. 10]</td>
</tr>
<tr>
<td>Ni 200</td>
<td>8.84</td>
<td>8.89</td>
<td>0.56%</td>
<td>58.71</td>
<td>Ni: 99.4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C,Cu,Fe,Mn,S,Sl: each ≤ 0.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Ref. 14]</td>
</tr>
<tr>
<td>TiC/Ni</td>
<td>4.8</td>
<td>5.42</td>
<td>11.44%</td>
<td>59.8</td>
<td>TiC: 77.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ni: 9.7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>WC: 11.9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Co: 1.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(own EDXS analysis)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Physical Characteristics of Anode Materials
B. Toolpieces

All toolpieces used were of cylindrical configuration, with the exposed electrode surface made of brass or copper, and insulated elsewhere with several coatings of KYNAR, a vinylidene fluoride resin (see Appendix II for procedure). The thickness of the KYNAR insulation was about 0.01 inch. Preliminary experiments were performed with toolpiece A, which had a brass electrode face with one large hole in the center for the electrolyte to pass through. Subsequent experiments were performed with toolpieces B and C, both of which had a copper electrode face with five small feed holes for the electrolyte; they are shown in Fig. 2.

The dimensions and surface areas of the toolpieces are listed in Table 2. Details of toolpiece construction have been given elsewhere. 7

C. Electrolyte

A variety of electrolytes have been used in the field for ECM work, including the sodium and potassium salts of such anions as chloride, bromide, sulphate, nitrate, chlorate, and perchlorate, also acid solutions such as HCl and H₂SO₄, and alkaline solutions of NaOH or KOH.²

In this study, a 2 M potassium nitrate solution was used throughout. This electrolyte is intermediate in cost and in the quality of surface finish it gives to the workpiece, compared to some electrolytes, such as chlorate solutions, which tend to give a very good surface finish, but are expensive, or chloride solutions, in which the aggressive nature of the halide ion tends to produce rough, pitted surfaces. The choice of KNO₃ also follows precedent of previous work on titanium carbide.⁷
Fig. 2. (a) Toolpieces B and C, used in this work. (b) Close-up of toolpiece electrode face.
Table 2: Toolpiece Dimensions

<table>
<thead>
<tr>
<th>Tool</th>
<th>Material</th>
<th>Number of Holes</th>
<th>Hole Diameter</th>
<th>Electrode Diameter</th>
<th>Toolpiece Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Brass</td>
<td>1</td>
<td>0.381 cm</td>
<td>0.635 cm</td>
<td>0.203 cm²</td>
</tr>
<tr>
<td>B</td>
<td>Copper</td>
<td>5</td>
<td>0.102</td>
<td>0.666</td>
<td>0.307</td>
</tr>
<tr>
<td>C</td>
<td>Copper</td>
<td>5</td>
<td>0.124</td>
<td>0.671</td>
<td>0.292</td>
</tr>
</tbody>
</table>
IV. Experimental Equipment and Procedure

A. ECM Equipment

The experimental equipment used in this study has already been described in detail by Riggs and Dissaux. Figure 3 is a photograph showing (from left to right) the chart recorder, the power supply, and the ECM cutting chamber. The electrolyte recirculation system lies further to the right.

The set-up is depicted more completely in the schematic diagram (Fig. 4), which centers around a job shop gun drill manufactured by the Hanson-Van Winkle-Munning Company. The equipment includes a small cutting chamber (a), 46x40x40 cm, with a stand (b) for mounting the work-piece (c), and a feed ram (d) with a range of advancement speeds, to which the toolpiece (e) is attached.

The power supply (f) delivers up to 30 volts at 500 amperes DC and has a large capacitor (300,000 mF at 500 volts) installed across the output terminals for the purpose of reducing ripple.

In the recirculation system, the electrolyte is pumped from the feed tank (g) by a 3 h.p. centrifugal feed pump (h). Passing through a filter (i) and a magnetic flow meter (j), the solution enters the cutting chamber, passes between the electrodes and drains to the storage tank (k). A 1/5 h.p. recycle pump (l) transfers the electrolyte to the feed tank.

Both tanks are equipped with filtering trays (m), in which Owens-Corning R-19 fiberglass insulation is used to filter the metal hydroxide out of the solution. The pressure of the electrolyte is measured by means of a strain gauge pressure transducer (n), and a pair of
Fig. 3. Experimental equipment. From left to right: chart recorder, power supply, ECM cutting chamber.
thermistors (p) are used to measure the electrolyte temperature before and after the machining gap.

The data recording system has digital displays for pressure, voltage and current, as well as a multi-channel strip recorder which records six variables in a semi-continuous manner (one data point printed in each channel every six seconds). The six variables measured are flow rate, current, electrolyte pressure, voltage, electrolyte temperature, and feed ram position.

B. ECM Run Procedure

Before each set of experiments on any given day, the specific gravity of the potassium nitrate electrolyte was adjusted to 1.1200, corresponding to a 2-molar concentration of KNO₃. Then the toolpiece was mounted on the feed ram, and the power was turned on. For each experimental run, the following procedure was used.

1. Before ECM run
   - rinse workpiece sample with water, then acetone
   - allow sample to dry for 5 minutes
   - weigh sample
   - clamp workpiece to anode platform in cutting chamber
   - polish tip of toolpiece with #600 abrasive paper
   - set initial starting gap between the electrodes, using a 25-mil-thick brass shim
   - set dial indicator for feed ram position at -25 mils
   - set thermistor inside cutting chamber to intercept electrolyte spray from machining gap
   - wet down rubber seal of door and clamp door shut
   - set applied voltage on powerstat of power supply
- set feed rate of toolpiece feed ram
- check all valves
- turn on chart recorder
- stir electrolyte solution
- measure temperature and specific gravity of electrolyte
- turn on feed pump and allow electrolyte to flow through system for one minute
- switch on the voltage and the toolpiece feed rate to start the run

2. During ECM Run

As a back-up to the chart-recorded data, the following variables were recorded by hand, as well, every 30 seconds: time, pressure, voltage, current, and toolpiece advancement. In addition, the electrolyte flow rate was monitored using flow into a 1-liter beaker and a stopwatch. The two sets of data matched quite well.

At the end of the experimental run, the electrolyte feed pump, the voltage, and the toolpiece advancement were turned off simultaneously with one switch.

3. After ECM Run
- measure electrolyte temperature, using solution remaining in the 1-liter beaker
- measure specific gravity of electrolyte
- record final toolpiece feed ram position
- remove workpiece sample from cutting chamber and rinse with water, then with acetone
- allow sample to dry for 5 minutes
- weigh sample
- transfer electrolyte from storage tank to feed tank for next experimental run (through glass wool filter)
- measure depth and diameter of hole drilled in workpiece

After each set of runs, everything was turned off, the toolpiece was removed from the feed ram and rinsed (see Fig. 5), and the electrolyte flow lines and the ECM cutting chamber were rinsed thoroughly with low conductivity water which was then discarded.

C. Estimate of Experimental Error

The estimates of the absolute and relative errors of the experimental parameters are shown in Table 3. From these values, the relative errors for the combined parameters have been determined and are listed in Table 4.

D. Surface Analysis Instruments

After machining holes in the three materials of interest, the surfaces at the bottom of the holes were investigated with several different instruments.

Surface appearance was viewed by means of an AMR Model 1000 scanning electron microscope (SEM), manufactured by the Advanced Metals Research Corporation. Energy dispersive X-ray spectrometry (EDXS) was used in conjunction with the SEM to determine surface compositions; the instruments for EDXS were a model 711 X-ray analyzer, made by EDAX International, Incorporated, and a model 7000 X-ray analyzer, manufactured by the Kevex Corporation.

Auger electron spectroscopy (AES) was used not only to determine surface compositions, but also to obtain composition depth profiles.
Fig. 5. Rinsing toolpiece after ECM.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Range of Values</th>
<th>Absolute Error</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied Voltage</td>
<td>V</td>
<td>10-25 volts</td>
<td>0.1 volt</td>
<td>0.4-1%</td>
</tr>
<tr>
<td>Time</td>
<td>t</td>
<td>1-15 min</td>
<td>2 sec</td>
<td>0.2-3%</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>Q</td>
<td>1-8 lit/min</td>
<td>0.05 lit/min</td>
<td>0.6-5%</td>
</tr>
<tr>
<td>Pressure</td>
<td>P</td>
<td>75-85 psig</td>
<td>0.5 psig</td>
<td>0.6%</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>S</td>
<td>1.11-1.12</td>
<td>0.0005</td>
<td>0.05%</td>
</tr>
<tr>
<td>Initial Temperature</td>
<td>ti</td>
<td>22-33°C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average Temperature</td>
<td>ta</td>
<td>22-33°C</td>
<td>0.1°C</td>
<td>0.1°C</td>
</tr>
<tr>
<td>Average Current</td>
<td>Ia</td>
<td>8-40 A</td>
<td>0.5 A</td>
<td>0.6-1%</td>
</tr>
<tr>
<td>Final Current</td>
<td>If</td>
<td>8-41 A</td>
<td>0.1 A</td>
<td>0.2-1%</td>
</tr>
<tr>
<td>Mass Loss</td>
<td>Δm</td>
<td>0.2-3.7 g</td>
<td>0.0002 g</td>
<td>0.2-3%</td>
</tr>
<tr>
<td>Starting Gap</td>
<td>SG</td>
<td>20-3000 mils</td>
<td>1 mil</td>
<td>0.2-3%</td>
</tr>
<tr>
<td>ECM Hole Depth</td>
<td>h</td>
<td>0.7-0.8 cm</td>
<td>0.005 cm</td>
<td>0.6-0.7%</td>
</tr>
<tr>
<td>ECM Hole Diameter</td>
<td>d</td>
<td>50-450 mils</td>
<td>0.5 mil</td>
<td>0.1-1%</td>
</tr>
<tr>
<td>Tool Advancement</td>
<td>δ</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4: Errors Resulting from Combined Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Equation</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Rate</td>
<td>Fr</td>
<td>Fr = δ/τ</td>
<td>0.1-2%</td>
</tr>
<tr>
<td>Machining Gap</td>
<td>2</td>
<td>2 = SG + h - δ</td>
<td>2-10%</td>
</tr>
<tr>
<td>Cross-sectional Area</td>
<td>a</td>
<td>a = π(d/2)^2</td>
<td>2-3%</td>
</tr>
<tr>
<td>Average Current Density</td>
<td>i_a</td>
<td>i_a = I_a/a</td>
<td>3-9%</td>
</tr>
<tr>
<td>Final Current Density</td>
<td>i_f</td>
<td>i_f = I_f/a</td>
<td>2-4%</td>
</tr>
<tr>
<td>Electrolyte Conductivity</td>
<td>k</td>
<td>*</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Ohmic Drop</td>
<td>V_{ir}</td>
<td>V_{ir} = i_f 2/k</td>
<td>4-15%</td>
</tr>
<tr>
<td>Overvoltage</td>
<td>n</td>
<td>n = V-V_{ir}</td>
<td>5-16%</td>
</tr>
<tr>
<td>Valence of Dissolution</td>
<td>z</td>
<td>z = (ItM)/(FΔm)</td>
<td>3-5%</td>
</tr>
<tr>
<td>ECM Driving Force</td>
<td>d.f.</td>
<td>d.f. = k V_{ir}/Fr</td>
<td>1-4%</td>
</tr>
<tr>
<td>Mass Removal Rate</td>
<td>m</td>
<td>m = Δm/τ</td>
<td>0.2-3%</td>
</tr>
<tr>
<td>Volume Removal Rate</td>
<td>V_{Vol}</td>
<td>V_{Vol} = m/ρ</td>
<td>0.2-3%</td>
</tr>
</tbody>
</table>

*See pages 14-15 for derivation of equation.
The AES instrument was a model 590 scanning Auger microprobe, made by Physical Electronics Industries, Inc.
V. Results

A. ECM Behavior

For each of the three materials studied, titanium carbide, nickel, and cemented titanium carbide/nickel (90/10), a set of ECM runs were performed over a range of conditions. The system parameters that were varied independently were the applied voltage and the toolpiece advancement rate.

Figure 6 shows a sample of each workpiece material with electrochemically drilled holes in it. Tables A1-A9 in Appendix III list the experimental conditions and results, and the derived parameters for the runs performed on each material.

1. Titanium Carbide

a. Valence of Dissolution

Values for the valence of dissolution in the ECM of titanium carbide were determined in three ways. First, the valence was calculated for each ECM run using equation (2):

\[
z = \frac{I \times M}{F \Delta m}
\]

and all the individual values were averaged to give \(\bar{z} = 6.7 \pm 0.3\) eq/gmol.

Using data from all the runs, two plots were made, \(\dot{m}\) vs. \(I\) and \(F_r\) vs. \(i\), and values for \(z\) were derived from the slopes in equations (3) and (5):

\[
\dot{m} = \left(\frac{M(60)}{F z}\right) I
\]

\[
F_r = \left(\frac{M(60)}{F z \rho}\right) i
\]
Fig. 6. View of anodes after electrochemical drilling. From left to right: TiC, Ni 200, TiC/Ni.
The factor 60 has been introduced for conversion from minutes to seconds. The values for current and current density used in these correlations are the average ones for each run, \( I_a \) and \( i_a \), respectively.

The plots are shown in Figs. 7 and 8; straight lines have been fitted to the experimental data points by linear regression. In addition, theoretical lines have been calculated for specific valences of dissolution, using equations (3) and (5). Both plots show that the experimental data lie between the 6- and 8-electron dissolution processes. The values for \( z \) obtained from the slopes of the experimental lines are shown in Table 5.

The two results for \( z \) agree well within experimental error, and the approximate error on their averaged value is only ± 3%. The value of 6.7 eq/gmol for \( \bar{z} \), mentioned above, also falls within this error limit.

b. Current-Voltage Relationship

Plotting cell voltage versus current density yields a straight line for TiC. Such a plot must be made for a specific ohmic drop through the electrolyte, so only data with the same interelectrode gap should be plotted together. The current-voltage relationship for a gap of 23 mils is shown in Fig. 9. Since the gap measured is that which occurs at steady-state conditions, the plot has been made using values of the final current density, \( i_f \), which is the steady current density maintained at the end of a run.

Figure 9 includes a theoretical line calculated for the ohmic drop through the solution at a gap of 23 mils, using equation (11):

\[
V_{Ir} = \frac{i}{k} \quad (11)
\]
Fig. 7. Mass removal rate versus current for TiC. Solid line: linear fit to experimental data. Dashed lines: theoretical correlations; 4-electron process (a), 6-electron process (b), 8-electron process (c).
Fig. 8. Toolpiece feed rate versus current density for TiC. Experimental and theoretical lines same as for Fig. 7.
Table 5. Apparent Valence Observed for TiC

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Slope</th>
<th>Valence(eq/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m vs. I</td>
<td>$5.638 \times 10^{-3}$</td>
<td>$6.61 \pm 0.11$</td>
</tr>
<tr>
<td>Fr vs. $i_f$</td>
<td>$1.149 \times 10^{-3}$</td>
<td>$6.57 \pm 0.21$</td>
</tr>
</tbody>
</table>

Average $z = 6.6 \pm 0.2$

($\overline{z} = 6.7 \pm 0.3$)
Fig. 9. Applied voltage versus current density for TiC in 2 M KNO₃, at an interelectrode gap of 23 mils.
in which a parallel-plate configuration is assumed. The electrolyte conductivity, \( k \), has been assigned a fixed value of \( 0.2 \, \Omega^{-1} \text{cm}^{-1} \).

The current-voltage curve lies above the ohmic drop line by about 4 volts. This difference is essentially constant over the range of current density investigated and is equal to the sum of the thermodynamic equilibrium potential and the overvoltages, \( \eta \), as defined in equation (12):

\[
V - V_{ir} = \eta = E_o + \eta_a + \eta_c + \eta_r
\]  

(12)

Combining this equation with equation (11) gives:

\[
\eta = V - V_{ir} = V - \frac{i \rho}{k}
\]  

(29)

Values for \( \eta \) have been calculated for each ECM run, using equation (29), and they are plotted versus current density in Fig. 10. There does not seem to be any obvious dependence of \( \eta \) on \( i_f \); the average value is 4.19 volts. The large scatter of data around \( \eta \) is probably related to the relative error for \( \eta \), which has been estimated to be \( \pm 5-16\% \) (see Table 4). While the values obtained for \( \eta \) are not very precise, they do give an estimate of its magnitude.

c. Interelectrode Gap Correlations

The dependence of the interelectrode gap on the ECM driving force was investigated in several ways. According to the theoretical equation developed in Chapter II, a linear relation is expected:

\[
\varepsilon = \left( \frac{M}{F \, z \, \rho} \right) \left( \frac{k \, V_{ir}}{Fr} \right) = \alpha \, (\text{d.f.})
\]  

(16)

In Fig. 11, a plot of gap versus driving force shows that the experimental data do follow a straight line, which has the following form:
Fig. 10. Values of $\eta$ versus current density for TiC. Solid line represents average value, $\overline{\eta}$. 

$\overline{\eta} = 4.19 \, \text{v}$
Fig. 11. Interelectrode gap versus ECM driving force for TiC.
The scatter of data in Fig. 11 is relatively low, indicating that this equation can be used to estimate the gap that will be obtained at a particular set of operating conditions. It must be noted, however, that since the values of d.f. which are to be plugged into equation (30) are calculated by means of the following relation:

\[ \text{d.f.} = \frac{k(V - \eta)}{Fr} \]  

(31)

a value for \( \eta \) must first be determined or assumed. The fact that for the case of TiC \( \eta \) seems to be a constant simplifies matters greatly.

The dependence of gap size on operating conditions can be demonstrated in another way, by plotting \( \lambda \) vs. \( i_f \) for specific applied voltages (see Fig. 12). The experimental data points have been plotted in four sets, corresponding to four voltages. The solid lines in the figure have been calculated for each value of applied voltage from the following equation, derived from Ohm's Law:

\[ \lambda = \frac{k(V - \eta)}{i_f} \]  

(32)

For the calculated correlations, the electrolyte conductivity, \( k \), is assigned a fixed value of 0.2 \( \Omega^{-1} \text{cm}^{-1} \), and \( \eta \) is assumed to have a constant value of 4.0 volts.

The experimental points follow the calculated curves fairly well; most of the deviation falls within experimental error limits. It should be noted that when the curves are calculated with the assumption that \( \eta = 0 \), they all lie shifted up to the right and do not match the experimental data at
Fig. 12. Interelectrode gap versus current density at different applied voltages for TiC. Solid curves represent calculated correlations for the values of applied voltage.
all. For the case of titanium carbide, then, $\eta$ is not a negligible quantity.

A graph similar to that in Fig. 12 is shown in Fig. 13; here, the gap has been plotted versus toolpiece feed rate, instead of against current density, but again for four values of applied voltage. The solid lines have been calculated from equation (16):

$$z = k \frac{(V - \eta)}{Fr} \frac{A(60)}{Fr \rho z}$$

where 60 has been introduced as a conversion factor from minutes to seconds, and values of $0.2 \, \Omega^{-1} \, \text{cm}^{-1}$ and 4.0 volts have been assigned to $k$ and $\eta$, respectively, as before.

The comparison between experimental points and calculated curves is essentially the same as for Fig. 12. Here, however, one can directly see the dependence of the interelectrode gap on the operating parameters which are controlled in ECM.

2. Nickel

a. Valence of Dissolution

The valence of dissolution for nickel 200 was first determined by averaging the values calculated for each ECM run, using equation (2). The average turned out to be $\bar{z} = 3.1 \pm 0.2 \, \text{eq/gmol}$.

To obtain values for $z$ by other means, the experimental data were plotted in two ways, as $i$ vs. $I$ and as $Fr$ vs. $i_f$. The two plots are shown in Figs. 14 and 15. Straight lines have been fitted to the experimental data, using linear regression. In addition, theoretical lines for specific valences of 2, 3 and 4 have been calculated from equations (3) and (5). These are shown as dashed lines in the figures.
Fig. 13. Interelectrode gap versus toolpiece feed rate at different applied voltages for TiC. Solid curves represent calculated correlations for the values of applied voltage.
Fig. 14. Mass removal rate versus current for Ni 200. Solid line: linear fit to experimental data. Dashed lines: theoretical correlations; 2-electron process (a), 3-electron process (b), 4-electron process (c).
Fig. 15. Toolpiece feed rate versus current density for Ni 200. Experimental and theoretical lines same as for Fig. 14.
From the slopes of the fitted lines, values for $z$ have been backed out in the same way as for TiC; they are shown in Table 6. While the agreement between these $z$ values is excellent, their estimated error ($\pm 10\%$) is high. The scatter of experimental points for nickel in Figs. 14 and 15 is higher than that for the data in the equivalent plots for TiC (Figs. 7 and 8); this contributes to the higher error in the case of the $z$ values for nickel. The value of 3.1 eq/gmol determined for $\bar{z}$ falls within this error limit.

b. Current-Voltage Relationship

A plot of cell voltage versus current density, shown in Fig. 16, indicates a linear relationship for nickel 200, as was the case for TiC. All the data shown corresponds to an interelectrode gap of 23 mils.

The dashed line in Fig. 16 represents the theoretical correlation for the ohmic drop through the solution, at a gap of 23 mils. The line has been calculated using equation (11), in which a value of 0.2 $\Omega^{-1}cm^{-1}$ has been assigned to $k$.

Unlike the case for TiC, the current-voltage curve and the ohmic drop line for nickel are not parallel; the difference between them ranges from 0-4 volts. Due to the experimental error associated with the data points ($\pm 2-4\%$ on $i_f$), it is difficult to draw significant conclusions.

Values of $\eta$ were calculated for each ECM run and they are plotted against $i_f$ in Fig. 17. If $\eta$ were truly inversely dependent on $i_f$, as suggested in Fig. 16, one would expect evidence of this in Fig. 17. However, no trend is apparent; the scatter appears to be large and random. The average value, $\bar{\eta} = +0.69$ volts, is shown on the plot as a horizontal line. The magnitude of $\bar{\eta}$ for nickel is small compared to $\bar{\eta}$ for TiC.
Table 6. Apparent Valence Observed for Ni 200.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Slope</th>
<th>Valence(eq/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \dot{m} ) vs. ( I )</td>
<td>( 13.217 \times 10^{-3} )</td>
<td>( 2.76 \pm 0.30 )</td>
</tr>
<tr>
<td>( F_r ) vs. ( i_f )</td>
<td>( 1.488 \times 10^{-3} )</td>
<td>( 2.76 \pm 0.26 )</td>
</tr>
</tbody>
</table>

Average \( z = 2.8 \pm 0.3 \)

\( (\bar{z} = 3.1 \pm 0.2) \)
Nickel 200
E.C.M. gap = 23 mil

Fig. 16. Applied voltage versus current density for Ni 200 in 2 M KNO₃, at an interelectrode gap of 23 mils.
Fig. 17. Values of $\eta$ versus current density for Ni 200. Solid line represents average value, $\bar{\eta}$.
c. Interelectrode Gap Correlations

A plot of gap versus ECM driving force for nickel 200 is shown in Fig. 18. A straight line of the form:

\[ z = 0.435(d.f.) + 3.21 \]  \hspace{1cm} (33)

has been fitted to the experimental data points by linear regression.

The scatter of data in this plot is higher for nickel than for TiC, rendering equation (33) less reliable as a means of estimating a priori the gap that will be obtained for a specific set of operating parameters.

The dependence of gap size on operating conditions for the case of nickel is illustrated in the next two figures. In Fig. 19, gap has been plotted against current density for four specific cell voltages. Figure 20 shows gap versus toolpiece feed rate for the four voltages. The curves in the figures represent theoretical correlations which have been calculated using equations (32) and (16). The value assigned to \( n \) in these calculations is 0.7 volts, and, despite the large variation in values obtained for \( n \) in the case of nickel (see Fig. 17) the calculated curves in Figs. 19 and 20 seem to fit the experimental points reasonably well.

3. Titanium Carbide/Nickel

a. Valence of Dissolution

For each ECM run on TiC/Ni, the valence of dissolution was calculated by means of equation (2). The average of all the values is \( \bar{z} = 6.7 \pm 0.2 \) eq/gmol.

Values for \( z \) were obtained graphically as well, by plotting \( m \) vs. \( I \) and \( Fr \) vs. \( i_f \) (Figs. 21 and 22). In each figure a straight line has been fitted to the experimental points by linear regression. The three dashed lines represent correlations for specific valences of dissolution, calculated by means of equations (3) and (5). The values for \( z \) have been backed
Fig. 18. Interelectrode gap versus ECM driving force for Ni 200.
Fig. 19. Interelectrode gap versus current density at different applied voltages for Ni 200. Solid curves represent calculated correlations for the values of applied voltage.
Fig. 20. Interelectrode gap versus toolpiece feed rate at different applied voltages for Ni 200. Solid curves represent calculated correlations for the values of applied voltage.
Fig. 21. Mass removal rate versus current for TiC/Ni.
Solid line: linear fit to experimental data.
Dashed lines: theoretical correlations; 4-electron process (a), 6-electron process (b), 8-electron process (c).
Fig. 22. Toolpiece feed rate versus current density for TiC/Ni.
Experimental and theoretical lines same as for Fig. 21.
out from the slopes of the fitted curves, and they are listed in Table 7.

The agreement between the graphically-obtained z values is not very good; however, the gap between them is adequately bridged by the experimental error. Because of this poor agreement, the average z has been recalculated to include $\bar{z}$, giving a new average value of 6.5, instead of 6.4 eq/gmol (see Table 7). This valence for TiC/Ni falls between those obtained for TiC (6.6) and for Ni (2.8); it is only a little smaller than the z for TiC.

b. Current-Voltage Relationship

A plot of cell voltage versus current density for TiC/Ni is shown in Fig. 23, for an interelectrode gap of 30 mils. As in the case of TiC and Ni 200, straight-line behavior is observed for TiC/Ni also.

The dashed line in the figure has been calculated for the ohmic drop through the electrolyte at a gap of 30 mils, using equation (11). As before, a value of 0.2 $\Omega^{-1} \text{cm}^{-1}$ has been assigned to $k$ in the equation.

The difference between the current-voltage curve and the ohmic drop line, defined as $\eta$, remains at approximately the same value of 3 volts over the entire range of current density investigated. This behavior is similar to that of pure TiC.

Values of $\eta$, calculated for each ECM run using equation (29), are plotted against current density in Fig. 24. The scatter of the data points is substantial, but not as large as in Fig. 17 for nickel. No dependence of $\eta$ on $i_f$ is apparent for TiC/Ni; this matches the results for TiC and Ni.

The horizontal line in Fig. 24 represents $\bar{\eta}$, calculated to be 2.95 volts. This average value is intermediate to those obtained for TiC
Table 7. Apparent Valence Observed for TiC/Ni.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Slope</th>
<th>Valence(eq/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m vs. I</td>
<td>$5.633 \times 10^{-3}$</td>
<td>$6.60 \pm 0.35$</td>
</tr>
<tr>
<td>Fr vs. $i_F$</td>
<td>$1.231 \times 10^{-3}$</td>
<td>$6.29 \pm 0.48$</td>
</tr>
</tbody>
</table>

Average $z = 6.4 \pm 0.5$

Average $z$, including $\bar{z} = 6.5 \pm 0.5$

($\bar{z} = 6.7 \pm 0.2$)
Fig. 23. Applied voltage versus current density for TiC/Ni in 2 M KNO₃, at an interelectrode gap of 30 mils.
Fig. 24. Values of $\eta$ versus current density for TiC/Ni. Solid line represents average value, $\overline{\eta}$. 

$\overline{\eta} = 2.95 \text{v}$
(4.19 v) and nickel (0.69 v), and it lies closer to the former.

c. Interelectrode Gap Correlations

The relationship between gap and ECM driving force for TiC/Ni is shown in Fig. 25 and appears to be linear. The line in the figure has been fitted to the experimental points by linear regression; it is described by the following equation:

\[ \lambda = 0.399 (\text{d.f.}) + 0.889 \]

The scatter of TiC/Ni data in Fig. 25 is moderate and intermediate to the scatter observed for TiC and for nickel (see Figs. 11 and 18). Equation (34), then, should be an acceptable means of estimating a priori the gap obtained at specific operating conditions. In particular, the estimate of gap size should improve at lower d.f. values, where the scatter in Fig. 25 is lower.

The dependence of gap size on operating conditions is demonstrated in two additional ways, by plotting \( \lambda \) vs. \( i_f \) (Fig. 26) and \( \lambda \) vs. \( F_r \) (Fig. 27), both for specific cell voltages. The four theoretical curves in each figure have been calculated using equations (32) and (16), in which a value of 3.0 volts has been assigned to \( \eta \). The fit of the theoretical curves to the experimental data points is somewhat worse for TiC/Ni than for the other materials investigated. Specifically, some of the data corresponding to cell voltages of 20 to 24 volts lie well below the lines. This divergence can be explained by the fact that the \( \eta \) values for these data are all significantly larger than \( \bar{\eta} \), which is 3.0 volts.
Fig. 25. Interelectrode gap versus ECM driving force for TiC/Ni.
Fig. 26. Interelectrode gap versus current density at different applied voltages for TiC/Ni. Solid curves represent calculated correlations for the values of applied voltage.
Fig. 27. Interelectrode gap versus toolpiece feed rate at different applied voltages for TiC/Ni. Solid curves represent calculated correlations for the values of applied voltage.
4. Comparative Behavior of Anode Materials

The ECM behavior of cemented TiC/Ni (90/10) appears to be dependent on that of its components, in that the $z$ and $n$ values for TiC/Ni are intermediate to those for TiC and nickel, as illustrated in Table 8.

It can be seen that the TiC/Ni values are closest to those for pure TiC, which is the major component in the composite.

All three anode materials exhibit straight-line behavior for both the current-voltage relationship and the gap-ECM driving force correlation. The behavior in the plots of $z$ vs. $i_F$ and $z$ vs. $F_r$ is also similar for all three materials.

In examining the electrochemical machining of cemented TiC/Ni in the light of its components, an important factor to consider is the comparison between machining rates. Since the densities of the anode materials are different, a comparison between mass removal rates, $\dot{m}$, would not be a direct one. Instead, it is more useful to look at the comparative volume removal rates.

To derive an expression for volume removal rate, $V_{\text{vol}}$, one first combines the following two equations:

\[ V_{\text{ir}} = V - n = \frac{I \cdot z}{a \cdot k} \quad (11) \]

and

\[ I = \frac{\dot{m} \cdot F \cdot z}{M} \quad (3) \]

to obtain:

\[ V - n = \dot{m} \left( \frac{F \cdot z \cdot a}{M \cdot a \cdot k} \right) \quad (35) \]
Table 8. Comparative \( z \) and \( n \) Values.

<table>
<thead>
<tr>
<th>Anode Material</th>
<th>( z ) (eq/gmol)</th>
<th>( n ) (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>6.6</td>
<td>4.2</td>
</tr>
<tr>
<td>TiC/Ni</td>
<td>6.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Ni 200</td>
<td>2.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>
The relation between mass removal rate and volume removal rate is simply:

\[ \dot{m} = \rho \dot{V} \text{Vol} \]  \hspace{1cm} (36)

Combining equations (34) and (36), and rearranging yields an expression relating cell voltage and volume removal rate:

\[ V = \dot{V} \text{Vol} \left( \frac{F z \rho \rho}{M a k (60)} \right) + \eta \]  \hspace{1cm} (37)

Note that 60 has been introduced as a conversion factor from minutes to seconds.

For each anode material, a plot has been made which illustrates the relationship between \( V \) and \( \dot{V} \text{Vol} \) demonstrated in equation (37). Each plot displays two sets of data, corresponding to two different interelectrode gaps. The TiC data have been plotted for gap sizes of 13 and 23 mils (Fig. 28), while the gap sizes for nickel 200 are 23 and 33 mils (Fig. 29). Figure 30 for TiC/Ni shows data for gaps of 15 and 30 mils. The gap sizes are not the same for all three materials, because it was not possible in this study to predict very closely the gap that would be obtained for a given set of operating conditions. Therefore, data were grouped by gap size after performing all the runs, and Figs. 28-30 correspond to the best of these groups of data.

All three figures illustrate the effect of gap size on the relationship between \( V \) and \( \dot{V} \text{Vol} \): at a given cell voltage, the volume removal rate increases as the gap size decreases.

Based on equation (37), the two lines in each of Figs. 28-30 should intersect at the y-axis, and this y-intercept should be equal to \( \eta \) for that material. However, none of the materials investigated follows this
Fig. 28. Applied voltage versus volume removal rate for TiC, at two different interelectrode gaps (13 and 23 mils).
Fig. 29. Applied voltage versus volume removal rate for Ni 200, at two different interelectrode gaps (23 and 33 mils).
Fig. 30. Applied voltage versus volume removal rate for TiC/Ni, at two different interelectrode gaps (15 and 30 mils).
expected behavior very closely. Some of the deviation is attributable to experimental error. Another factor to consider is that at 10 volts applied voltage the ECM system used in this study is close to its lower limit of operation. Therefore, the extension of the lines to the y-axis cannot be substantiated by experimental data at lower voltages.

The final objective of plotting V vs. V_0 for each anode material is to be able to compare their removal rates on the same basis. If, for a given set of ECM conditions, the volume removal rates for TiC and nickel are not the same, then one of the two phases in the TiC/Ni composite ought to dissolve preferentially to the other, resulting in a rough surface finish after ECM. However, if a set of ECM conditions can be found at which TiC and nickel have the same volume removal rate, then an optimum surface finish should be obtainable. To determine where this set of ECM conditions lies, one seeks a point at which the V vs. V_0 lines for TiC and nickel intersect.

Figures 28 and 29 each contain a line corresponding to a gap of 23 mils; these lines, if superimposed, would intersect at a point just above 11 volts. However, due to the deviation of the nickel 200 line from the behavior expected in equation (37), firm conclusions about this point of intersection cannot be drawn.

In an attempt to circumvent this ambiguity, Fig. 31 has been prepared, in which a hypothetical line has been calculated for each anode material by means of equation (37). The interelectrode gap for all three lines is 20 mils. In this plot the lines for TiC and for nickel do not intersect at all, suggesting that, in this system ECM conditions do not exist at which TiC and nickel exhibit the same volume
Fig. 31. Theoretical plot of applied voltage versus volume removal rate for each anode material (TiC, Ni 200, and TiC/Ni), at an interelectrode gap of 20 mils.
removal rate. However, the two lines are not exactly parallel; they approach each other as cell voltage decreases, indicating that preferential dissolution might be lower in this region, resulting in an improved surface finish.

The line calculated for TiC/Ni lies very close to the TiC line, intersecting it just above 12 volts. It seems that the behavior of TiC/Ni and TiC is similar; this is further supported by comparing the experimental lines for the two materials, shown in Figs. 28 and 30.

Although the difference between the slopes of the TiC and the TiC/Ni lines in Fig. 31 is noticeable, examination of equation (37) shows that some of its parameters, such as \( z \), \( p \), and \( a \), which are used to calculate the slope, have been experimentally determined. Therefore, the calculated lines in this figure are not entirely dependable. Rather, they serve only to suggest the general trends in behavior that the anode materials might exhibit.

B. Surface Analysis

A study was undertaken to evaluate the effect of different operating conditions on the surface appearance of the anodes. Surface morphology and relative roughness were observed by means of scanning electron microscopy (SEM). Bulk and surface compositions, as well as compositions of discrete regions on the materials, were determined by means of energy dispersive X-ray spectrometry (EDXS) and Auger electron spectroscopy (AES). Compositions resulting from different operating conditions were compared and evaluated for evidence of an oxide layer. The TiC/Ni surfaces were also analyzed for evidence of preferential dissolution of one phase.
1. Scanning Electron Microscopy: Surface Appearance

The surface appearances of the anodes before and after electrochemical machining were compared. Prior to ECM, the TiC and Ni 200 specimens had been cut and machined mechanically. Their surfaces were smooth, but not highly polished. Each TiC/Ni sample was made individually on site (see Appendix I), and ECM was at first performed on samples as obtained after the sintering step. However, EDXS and AES studies showed the composition of the outer layer of material to be different from the bulk composition, a common phenomenon in powder metallurgy. Consequently, the remaining TiC/Ni surfaces to be electrochemically machined were polished, using a diamond polishing wheel.

Figure 32 shows SEM micrographs of TiC and TiC/Ni surfaces before ECM, all taken at 2000X magnification. Titanium carbide exhibits a sharp-edged, semi-discontinuous appearance (Fig. 32a), suggesting TiC particles compressed into a unit. On the unpolished surface of the TiC/Ni composite (Fig. 32b), one can clearly see discrete chunks of material. The size of these chunks is on the average greater than that of the particles suggested in the TiC surface. Note also that the TiC/Ni surface is knobby, rather than sharp-edged.

Figure 32c shows a TiC/Ni surface after extensive polishing with a diamond wheel. Dark, angular chunks of material appear in a lighter-colored matrix. EDXS analysis indicates a higher Ti:Ni ratio in the darker regions than in the lighter ones, suggesting that the dark chunks are TiC-rich particles embedded in a nickel-rich matrix. The small black areas are presumed to be air-filled pores in the structure.
Fig. 32. SEM micrographs of anode surfaces before ECM: TiC (a), TiC/Ni as sintered (b), TiC/Ni after diamond polishing (c).
Typical post-ECM surfaces for the anode materials are shown in Fig. 33. All three micrographs were taken at 2000X magnification. The surface of TiC in Fig. 33a exhibits a particulate nature; however, it appears less sharp-edged than the surface before ECM. Moreover, a number of large, smooth regions are also apparent on this surface.

The appearance of the nickel and TiC/Ni surfaces is very different. Two kinds of region, light and dark, are observed optically, via SEM, on each surface. Looking at Fig. 33b, one can see a delicately-structured white substance that appears to be partially covering a darker, denser-looking material. The post-ECM nickel surface (Fig. 33c) is similar in appearance; however, the white material appears to have a very fine structure, and it covers the darker material more densely. The white substances observed on these nickel and TiC/Ni surfaces look as if they could be oxides.

For TiC and Ni 200, the post-ECM surfaces obtained at different ECM conditions did not exhibit much variation. For the TiC/Ni composite, however, a phenomenon which will be referred to as macro-roughness was observed on surfaces machined at lower values of applied voltage and toolpiece feed rate.

Figure 34 contains four SEM micrographs for TiC/Ni. The first two correspond to a typical post-ECM surface, which at 100X magnification (Fig. 34a) appears relatively smooth and at 1000X (Fig. 34b) shows clearly the light and dark phases discussed above. The second pair of micrographs correspond to a TiC/Ni specimen machined at V = 10 volts and Fr = 0.02 cm/min, which are the lowest values of these variables used in this study. In the micrograph taken at 100X (Fig. 34c), ridges are apparent, between which the surface is smooth. At the higher magnification, 1000X (Fig. 34d),
Fig. 33. SEM micrographs of typical post-ECII anode surfaces: TiC (a), TiC/Ni (b), Ni 200 (c).
(Machining conditions: V = 15 volts and F$_r$ = 0.05 cm/min.)
Fig. 34. SEM micrographs of post-ECNi TiC/Ni surfaces; (a) and (b): $V = 15$ volts, $F_r = 0.05$ cm/min; (c) and (d): $V = 10$ volts, $F_r = 0.02$ cm/min.
evidence of these ridges is not as clear; in general, the appearance is similar to the typical surface (Fig. 34b).

The ridges do not always occur across the entire surface at the bottom of an electrochemically-drilled hole. Often, patches of ridges appear in one region of the surface. The compositions of the two kinds of surface were analyzed by means of EDXS. The results are presented in the next section; they are discussed in terms of the different operating conditions.

2. Surface Composition
   a. Overall Composition

   EDXS spectra of post-ECM titanium carbide surfaces showed large peaks for Ti and only trace peaks of a few other elements, Fe and K. Note that neither carbon nor oxygen is detectable by EDXS. For nickel 200, only a nickel peak was observed.

   Analysis of surface composition was more complex for the TiC/Ni composite. At first, ECM was performed on TiC/Ni specimens as obtained after sintering. However, when EDXS spectra were taken to compare the original surface composition with that of the post-ECM surface, the results indicated that the original surface contained about 30 wt% nickel. Since the amount of nickel powder used in fabricating the TiC/Ni specimens was only 10%, it was concluded that, after sintering, the composition of the outer layer of material must have become different from that of the bulk.

   To confirm this hypothesis, four of the remaining TiC/Ni specimens were machined smooth on one side by means of a diamond wheel. EDXS analysis was then performed on both the polished and the unpolished sides. The results, listed in Table 9, show that the unpolished surfaces do indeed
Table 9. Compositions of Unpolished and Polished TiC/Ni Surfaces Determined by EDXS Analysis (Atomic Composition).

<table>
<thead>
<tr>
<th>Specimen #</th>
<th>Unpolished Surface</th>
<th>Polished Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%Ti</td>
<td>%Ni</td>
</tr>
<tr>
<td>2</td>
<td>71</td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>59</td>
<td>41</td>
</tr>
<tr>
<td>12</td>
<td>65</td>
<td>35</td>
</tr>
</tbody>
</table>

AVERAGE 70.75 29.25 88.75 11.25
have a much higher nickel content than does the bulk material. Moreover, the amount of nickel in the bulk is found to be 11%, which is close to the expected value of 10%. Note that, while the data in Table 9 have been presented as atomic % of Ti and Ni, the conversion to weight % TiC and Ni gives almost exactly the same numbers.

Post-ECM surfaces of TiC/Ni were analyzed by means of both EDXS and AES. It was possible to obtain EDXS spectra for surfaces machined at most of the operating conditions investigated, but very deep holes could not be examined, due to geometrical limitations of the technique. Compositions were determined for the general surface, unless two kinds of surface were observed. In the latter case, compositions were obtained for each region. Table 10 lists the values obtained for nickel content, in order of increasing cell voltage and toolpiece feed rate. There are separate columns for compositions of smooth and rough surfaces; where one kind of surface is less predominant, its symbol has been put in parentheses.

The data shown in Table 10 exhibit several trends. First, the amount of nickel observed for all of the post-ECM surfaces is clearly higher than the amount in the bulk material. This indicates preferential dissolution of the TiC phase over the Ni phase.

A second observation is that the smooth type of surface is more predominant than the rough type. Furthermore, the smooth regions contain more nickel than the rough ones. This is true not only in comparing the average compositions of the two surface types, but also for each pair of values for a particular set of operating conditions. The amount of nickel observed in the smooth surfaces ranges from 20 to 45%, with the peak value occurring at intermediate conditions (V = 20 volts, Fr = 0.05 cm/min).
Table 10. Nickel Content in Post-ECM TiC/Ni Surfaces, as Obtained by EDXS Analysis.**

<table>
<thead>
<tr>
<th>ECM Operating Conditions</th>
<th>Smooth Surface</th>
<th>%Ni</th>
<th>Rough Surface</th>
<th>%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before ECM</td>
<td>-</td>
<td>12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10 10</td>
<td>(S)</td>
<td>31</td>
<td>R</td>
<td>20</td>
</tr>
<tr>
<td>15 12</td>
<td>(S)</td>
<td>*</td>
<td>R</td>
<td>*</td>
</tr>
<tr>
<td>15 15</td>
<td>S</td>
<td>31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20 15</td>
<td>(S)</td>
<td>45</td>
<td>R</td>
<td>12</td>
</tr>
<tr>
<td>20 18</td>
<td>S</td>
<td>39</td>
<td>(R)</td>
<td>*</td>
</tr>
<tr>
<td>24 17</td>
<td>S</td>
<td>39</td>
<td>(R)</td>
<td>23</td>
</tr>
<tr>
<td>24 19</td>
<td>S</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24 20</td>
<td>S</td>
<td>28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24 24</td>
<td>S</td>
<td>23</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Data not available.

** The symbols for the surface types signify the following:

- S - smooth surface, predominant
- (S) - smooth surface, small region
- R - rough surface, predominant
- (R) - rough surface, small region
This variation does not seem to correlate in any meaningful way with the values of V and Fr. It is possible that some of the spread is due to lack of accuracy in the technique; differences in hole depth may have contributed to variations in composition.

Auger electron spectroscopy was used as an alternate technique to confirm the EDXS results. Several post-ECM surfaces were investigated; not only was the surface itself analyzed, but a composition profile was also obtained, by alternately sputtering away thin layers of material and analyzing for composition. Figures 35 and 36 together show such a profile for Run 26 (V = 15 volts, Fr = 0.05 cm/min). It traces the relative amounts of the major elemental components, titanium, nickel, carbon and oxygen. The total sputtering time is 16 minutes, corresponding to about 0.32 \( \mu \) of material removed. At the end of this time, the profiles of each element have begun to flatten out, indicating that the bulk composition of the TiC/Ni specimen has been reached.

The effect of ECM on surface composition can be evaluated from the initial composition observed in the TiC/Ni profile. The values for the initial amounts of each element have been read off the profile after the first sputtering interval, at 0.5 min, because the values at \( \tau = 0 \) are affected by a contamination overlayer. This film is commonly due to carbon and oxygen contamination and masks the other Auger signals until it has been sputtered off the surface.

Table 11 lists the initial and final amounts of each element shown in the profile. Nickel and oxygen start high at the surface and drop off into the bulk material, whereas titanium and carbon increase into the bulk. The initial value of 47% for Ni is higher than that obtained by EDXS, 31%,
Fig. 35. Composition profile of post-ECM TiC/Ni surface, obtained by AES. Part I. (Machining conditions: \( V = 15 \) volts, \( Fr = 0.05 \) cm/min).
Fig. 36. Composition profile of post-ECM TiC/Ni surface, obtained by AES. Part II.
(Machining conditions: $V = 15$ volts, $Fr = 0.05$ cm/min).
Table 11: Initial and Final Compositions Obtained from AES Profile of TiC/Ni.

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial Atomic %</th>
<th>Final Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>47</td>
<td>11</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>44</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>39</td>
</tr>
<tr>
<td>O</td>
<td>21</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
but both values are higher than the bulk, 11%. Note that the error associated with the AES analysis is 5% or higher, since the surfaces being examined are rougher than those usually studied by AES, and since sensitivity factors for quantitative analysis of this matrix are uncertain.

The amounts of Ti and C in the surface are initially low, but by the end of the profile they have risen to 44% and 39%, respectively. These values are not only close to each other, but also close to the expected value of 45% for both elements.

Oxygen is initially present at 21%, an amount substantial enough to suggest the presence of an oxide on the surface. However, the thickness of this oxide is probably much less than that suggested in the profile. Due to the roughness of the surface, the Argon ion beam, which comes in at an angle, is not able to sputter away the material evenly. Therefore, the analyzing beam, which is normal to the surface, will continue to detect any oxide that has been sheltered from the sputtering beam. The probable thickness of the oxide layer is less than 400 Å. Eventually, the amount of oxygen drops off to 6% in the bulk; this value is essentially negligible, since it is very close to the 5% error limit.

In conclusion, the AES results support the EDXS results and the observation that, in the electrochemical machining of TiC/Ni, the titanium carbide phase dissolves preferentially to the nickel phase. AES analysis also supports the idea of an oxide on the post-ECM surface.

b. Differentiation Between "Light" and "Dark" Phases

A detailed study was made on the post-ECM surfaces of nickel and TiC/Ni, to determine the nature of the two phases, which appear light and dark in the SEM micrographs, that were observed on each material.
In particular, further evidence was sought to confirm the hypothesis that the light substance is an oxide.

For nickel 200, the two phases were first examined by EDXS. Spectra were generated separately for each phase by focussing at high magnification (5000X) on different light and dark regions. Even though all the spectra exhibited a nickel peak only, differences could be observed in the peak heights displayed on the EDXS analyzer screen.

Table 12 lists the relative peak heights observed for each phase and gives the average values. The dark phase clearly shows a stronger nickel signal, at 93% of scale, than does the light phase (85%). Since the dark phase appears to be the underlying one, it is possible that some of the signal is lost in the recesses of the material. Therefore, the nickel peak for the dark phase ought perhaps to be even higher than it is.

The smaller nickel peaks observed for the light phase suggest that this material could be an oxide. This hypothesis is further supported by the AES results for nickel. Composition profiles were made for both the original surface and a post-ECM surface; these are shown in the next two figures. Both profiles trace the relative amounts of the main elements observed, nickel, oxygen and carbon. Note the different time scales.

In the profile of the original surface (Fig. 37), carbon and oxygen start out at levels greater than 30% (atomic composition), but after the first sputtering interval, they have dropped to well below 10%. As discussed previously, this behavior is typical of a contamination overlayer; therefore, the initial presence of carbon and oxygen is not considered significant. Furthermore, the residual levels of these elements is close
Table 12. Relative Ni Peak Heights in EDXS Spectra of Regions on a Post-ECM Surface of Nickel 200.

<table>
<thead>
<tr>
<th>Light Regions (% Scale)</th>
<th>Dark Regions (% Scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td>90</td>
</tr>
<tr>
<td>88</td>
<td>90</td>
</tr>
<tr>
<td>84</td>
<td>98</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>93</strong></td>
</tr>
</tbody>
</table>
Fig. 37. Composition profile of original Ni 200 surface, obtained by AES.
to the 5% error estimated for AES analysis.

Figure 38 shows the composition profile of a post-ECM nickel surface. Carbon and oxygen, as well as nickel, appear in this figure also, but their profiles differ from those for the original surface. The relative amounts of carbon and oxygen decrease gradually to the residual levels, suggesting that these elements are present as more than just surface contaminants.

Another important observation is that the initial drop-off rate of oxygen is lower than that of carbon. Thus, while carbon may still be a contaminant of some sort, the different behavior of oxygen indicates that it is not a similar contaminant, and that it may be present as part of an oxide layer. If this is indeed the case, one would expect the oxide to be one of nickel, and its thickness, determined from an approximate sputter rate of 200 Å/min and a sputter time of 2 minutes, would be 400 Å or 0.04 μ.

The TiC/Ni composite was also examined by means of EDXS and AES. EDXS analysis, combined with SEM, was especially instructive in studying the two phases in the post-ECM surfaces of this material. Since the EDXS spectra contained peaks for more than one element, X-ray mapping was possible.

Figure 39b shows an SEM micrograph of a post-ECM surface, taken at high magnification (5000X). Light and dark regions are clearly distinguishable. On the left is an X-ray map for titanium (Fig. 39a), and on the right is a map for nickel (Fig. 39c). This set of pictures shows qualitatively, but clearly, that the light regions are rich in nickel, while the dark regions are rich in titanium.
Fig. 38. Composition profile of post-ECM Ni 200 surface, obtained by AES (Machining conditions: \( V = 15 \) volts, \( F_r = 0.05 \) cm/min).
Fig. 39. (a) X-ray map for Ti, corresponding to (b); (b) SEM micrograph of post-ECM TiC/Ni surface; (c) X-ray map for Ni (Machining conditions: V = 15 volts, F = 0.05 cm/min).
Quantitative results were obtained by focussing on individual light and dark areas and determining their compositions from EDXS spectra. Table 13 summarizes the results for several smooth post-ECM surfaces. The nickel content of the light regions averages 49%, which is much higher than that of the general surface (28%). In contrast, the dark regions appear to contain an average of only 19% nickel.

Spectra of light and dark regions were also obtained in the AES studies done on TiC/Ni. A spectrum for a light region is shown in Fig. 40. One can see fairly large signals for nickel and oxygen, and moderate signals for titanium and carbon. In comparison, Fig. 41 for the dark region shows only a minimal signal for nickel. The titanium and oxygen peaks are slightly smaller in this spectrum, while the carbon peak is very large.

The large drop in the nickel signal from the light region to the dark correlates very well with the other evidence that indicates that the light phase is an oxide layer. The larger oxygen peak observed in the spectrum of the light region adds further support to this hypothesis.

It is difficult to draw conclusions about the relative peak sizes observed for titanium and carbon in the two spectra; the titanium signals are about the same, whereas the carbon peak is much larger in the spectrum for the dark region. It is possible that the roughness of the TiC/Ni surfaces is too great to allow very accurate analysis by scanning Auger techniques. TiC is the predominant component throughout the specimen; therefore, any imprecision in focussing on a particular region, or any undetected gaps in the overlying, light-colored phase would alter the titanium and carbon signals from those corresponding to the surface element considered.
Table 13. Nickel Content of Different Regions on Smooth, Post-ECM TiC/Ni Surfaces as Determined by EDXS (Atomic Composition).

<table>
<thead>
<tr>
<th>Run</th>
<th>General Surface, % Ni</th>
<th>Light Region</th>
<th>Dark Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>23</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>71</td>
<td>20</td>
<td>61</td>
<td>19</td>
</tr>
<tr>
<td>59</td>
<td>17</td>
<td>37</td>
<td>7</td>
</tr>
<tr>
<td>67</td>
<td>39</td>
<td>52</td>
<td>23</td>
</tr>
<tr>
<td>70</td>
<td>39</td>
<td>64</td>
<td>25</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>28</td>
<td>49</td>
<td>19</td>
</tr>
</tbody>
</table>
Fig. 40. AES spectrum of light-colored region on post-ECM TiC/Ni surface (Machining conditions: V = 15 volts, Fr = 0.05 cm/min).
Fig. 41. AES spectrum of dark-colored region on post-ECM TiC/Ni surface (Machining conditions: V = 15 volts, Fr = 0.05 cm/min).
VI. Discussion

The electrochemical machining of TiC/Ni (90/10) has been studied along with that of its components, titanium carbide and nickel, in order to compare the results obtained for the three materials and to explore the relationship between the composite and its components.

In investigating the ECM behavior of the three anode materials, apparent valences of dissolution were determined to be the following:

$$\begin{align*}
\text{TiC: } z &= 6.6 \text{ eq/gmol} \\
\text{TiC/Ni: } z &= 6.5 \text{ eq/gmol} \\
\text{Ni 200: } z &= 2.8 \text{ eq/gmol}
\end{align*}$$

The valence determined for TiC in this study agrees well with the value of 6.7 eq/gmol obtained earlier by Dissaux in this laboratory.\(^7\) Values ranging from 6.5 to 7.0 eq/gmol have been reported by Cowling and Hintermann; their results, obtained at much lower current densities (5 μA to 5 mA) and correspondingly lower voltages (1 volt), indicate a dependence of valence on voltage.\(^16\)

The anodic dissolution of nickel has been investigated by many authors; in particular, Datta and Landolt,\(^17\) and MacDougall\(^18\) assume that nickel dissolves to a divalent ion ($\text{Ni} \rightarrow \text{Ni}^{+2} + 2\text{e}^-$). An apparent valence larger than 2.0 suggests that the current efficiency of this reaction is less than 100%, probably due to concurrent oxygen evolution. Since oxygen evolution could not be monitored in the system used in this study, it was not possible to independently check the current efficiency of nickel dissolution.

As discussed in the previous chapter, the apparent valence of the TiC/Ni composite is intermediate to those of its components, and closest
to the value obtained for TiC, the major component. This intermediate behavior is also observed in comparing the values obtained for \( \eta \), defined as the sum of the thermodynamic equilibrium potential and the overvoltages:

\[
\begin{align*}
\text{TiC: } \eta &= 4.2 \text{ volts} \\
\text{TiC/Ni: } \eta &= 3.0 \text{ volts} \\
\text{Ni 200: } \eta &= 0.7 \text{ volts}
\end{align*}
\]

For all three materials, \( \eta \) remained constant, within experimental error, over the range of operating conditions investigated.

The ECM behavior of TiC/Ni was found to be similar to that of its components in other respects, as well. A straight-line relationship was observed in all the current-voltage and gap-ECM driving force correlations (see Figs. 9, 11, 16, 18, 23, 25). Also, all three materials exhibited similar behavior in the plots of \( \varepsilon \) vs. \( i_f \) and \( \varepsilon \) vs. \( F_p \).

While the TiC/Ni composite exhibits behavior which is qualitatively dependent on that of its components, the quantitative values for \( \varepsilon \) and \( \eta \) of TiC/Ni are not stoichiometrically intermediate to those of TiC and nickel. Therefore, based on the data obtained in this study, it is not possible to quantitatively predict these electrochemical parameters for TiC/Ni from those of TiC and nickel.

Surface analysis of the anode materials showed the TiC/Ni composite to be strongly affected by the presence of the nickel phase. While the post-ECM surface of TiC appeared bare of any oxide layer, both nickel and TiC/Ni exhibited a light-colored substance on the post-ECM surfaces, as seen in the SEM micrographs.
Evidence to identify these light-colored substances as oxides was sought by means of EDXS and AES. The results support the presence of a thin oxide layer on each material, but the evidence is not conclusive. This is partly due to limitations in the analytical techniques arising from high surface roughness of the specimens.

Anodic films on nickel have been studied extensively by Datta, Matthieu and Landolt.\textsuperscript{19} Using coulometry and AES, they detected a very thin oxide layer on nickel surfaces obtained after high-rate transpassive dissolution. The thickness of the film was estimated by means of AES to be 5-25 Å; the accuracy in this technique was limited.

The composition of the oxide formed on nickel surfaces after anodic dissolution has not been investigated in this study. MacDougall has studied oxides formed on nickel at voltages below one volt and proposes NiO as the oxide in the film.\textsuperscript{18} However, Datta, Matthieu and Landolt, whose work was done at higher voltages (1-4 V), suggest the presence of trivalent or even higher nickel oxides in the film.\textsuperscript{19}

Although in this study there was no oxide film suggested in the SEM micrographs of TiC after machining, several authors have detected TiO\textsubscript{2} films on Ti and TiC surfaces after anodic oxidation.\textsuperscript{7,20,21,22} Cowling and Hintermann have suggested that above 1.75 volts the film consists of the hydrated oxide, TiO\textsubscript{2}·H\textsubscript{2}O.\textsuperscript{22} It is possible that such an oxide layer is in fact present on the TiC surfaces investigated in this study, but it may be too thin to be detectable by means of SEM.

Based on the appearance of the post-ECM TiC/Ni surfaces in the SEM micrographs and on the high nickel content found at the surface by AES, it is likely that the oxide layer suspected to be on the surface is
largely composed of one or more nickel oxides. Titanium may also be present as an oxide, but it would only be a minor component.

Analysis of the surface composition of TiC/Ni showed an increase in nickel content after ECM, indicating preferential dissolution of the TiC phase during machining. This evidence of preferential dissolution was observed over the entire range of operating conditions employed. Although the nickel content varied somewhat from one post-ECM surface to another, no correlation with applied voltage or with toolpiece feed rate was apparent.

Similar results were obtained by Petit, et al., who studied the dissolution of single- and two-phase Ti-Cu alloys at voltages less than 1 volt. In these materials, titanium was found to dissolve preferentially, leaving the surface of the alloy enriched with copper. Bannard has studied the ECM of several commercial Ti alloys, some two-phase; his results indicate differential dissolution in the case of the two-phase materials. Moreover, all of the alloy surfaces obtained after machining were rough and dull; a polish regime for the alloys could not be identified.

While polished post-ECM surfaces for TiC/Ni were not obtained in this study, it may be possible to determine a polish regime for this material by using a system which allows a wider range of operating conditions, or by exploring different electrolytes and electrolyte combinations. In addition, a closer look at the overvoltage behavior and at the volume removal rates of each of the anode materials studied may improve the predictability of the ECM behavior of the TiC/Ni composite based on that of its components.
VII. Conclusions

The principal conclusions of this work can be summarized as follows:

1. The feasibility of electrochemically machining cemented titanium carbide (TiC/Ni) has been established.

2. The ECM behavior of TiC/Ni (90/10) is found to be qualitatively similar, but not stoichiometrically intermediate to that of its components, TiC and nickel.

3. The apparent valence of dissolution has been determined for each material and is found to be constant over the range of operating conditions investigated. The values obtained are TiC: 6.6, Ni: 2.8 and TiC/Ni: 6.5 eq/gmol.

4. Over the current density range investigated, all three materials exhibit linear dependence of current density on applied voltage.

5. For each material, the value of \( n \) appears to be nearly constant over the range of operating conditions employed. The values determined for \( n \) are 4.2, 0.7 and 3.0 volts for TiC, Ni and TiC/Ni, respectively.

6. Correlations relating the interelectrode gap to the independent operating parameters (applied voltage and toolpiece feed rate) have been obtained for all three materials. They appear to be adequate for a priori estimation of the gap size.

7. A light-colored substance is observed by means of SEM on the post-ECM surfaces of Ni and TiC/Ni, but not on TiC. EDXS and AES analysis suggest that this material is a nickel oxide layer. However, the evidence is not sufficient to be conclusive.
(8) Preferential dissolution of the TiC phase in the cemented TiC/Ni composite is observed over the entire range of operating conditions investigated.

(9) A polish regime for TiC/Ni (90/10) could not be identified in this ECM system.
References


Appendix I: Fabrication of Cemented TiC/Ni Specimens

The method used to fabricate cemented TiC/Ni was developed in the laboratory using various literature sources and advice from Kennametal Inc., Latrobe, Pennsylvania.

Titanium carbide powder, specified as -325 mesh and 99.5% pure, was obtained from Cerac, Inc. The nickel powder used was specified as -400 mesh and 99.99% pure; it was manufactured by the Bram Metallurgical-Chemical Co., Philadelphia, Pennsylvania. These powders were mixed in a ratio of 9:1 by weight. The mixture was ball-milled in hexane for 60 hours. The balls and lining of the ball mill were made of tungsten carbide.

After milling, the powder was spread out to air-dry and then placed in an oven at 100°C for final drying. The dry powder was put through a -100 mesh screen to break up the larger particles.

SEM micrographs of the powders are shown in Fig. A1. The TiC powder (Fig. A1a) appears prismatic and sharp-edged, while the nickel powder (Fig. A1c) looks knobby and multigranular. Note that the appearance of the TiC/Ni powder (Fig. A1b) is intermediate to that of its components; this corresponds to the fact that, after ball-milling, the titanium carbide particles are coated with nickel. From the micrographs, the average particle size for each powder appears to be 2μ, 1.5μ and 1μ for TiC, TiC/Ni and Ni, respectively.

To aid in cold-pressing, the TiC/Ni powder was waxed. This was accomplished by weighing out an amount of shaved paraffin corresponding to 2-3% of the weight of the powder, following which the paraffin was dissolved in benzene over very low heat on a hotplate. The powder was
Fig. A1. SEM micrographs of powders in ball-milling of TiC/Ni: (a) TiC powder, (b) TiC/Ni powder after milling, (c) Ni powder.
then added, and the slurry was stirred until the benzene had evaporated off, leaving the TiC/Ni powder coated with wax.

Specimens were pressed in a 3/4-inch diameter, cylindrical steel die. Teflon sleeves were used to prevent leakage of the powder. The pressure on the die was brought slowly up to 30,000 psi, held for a dwell time of 30 sec - 2 min, and released slowly. Before sintering, the top and bottom of each specimen were polished smooth with #600 abrasive paper.

Sintering was done in one of two high-vacuum resistance furnaces, manufactured by Brew and by the Abar Corporation; both furnaces used a tungsten mesh element. Specimens were sintered one or two at a time in an aluminum oxide crucible. A Pt-Pt + 10% Rh thermocouple was placed alongside the specimen in order to estimate the temperature inside the furnace. The following heating and cooling sequence was used:

- Pull a vacuum on the sample chamber.
- Heat from 0-800°C over 2-1/2 hours.
- Backfill chamber with helium.
- Heat from 800-1100°C over 2-1/2 hours.
- Heat from 1100-1370°C over 2-1/2 hours.
- Hold at 1370°C for 45-50 minutes to sinter. Keep temperature fluctuations within ± 6°C.
- Cool from 1370-0°C over 7-8 hours.

A volumetric shrinkage of 38% was observed after sintering. The final diameter of the specimens was approximately 0.65 inch.
Appendix II: KYNAR Coating of Toolpieces

The toolpieces used in this work were electrically insulated on the sides with KYNAR vinylidene fluoride resin, manufactured by the Pennsalt Chemicals Corporation, Philadelphia, Pennsylvania. The properties of this material include high dielectric strength, excellent abrasion resistance, toughness, temperature stability from -62°C to 150°C, resistance to most solvents and corrosive chemicals, and ease of application.\(^6\)

A grade 204 dispersion of KYNAR was applied by means of a spray gun. The following procedure was used:

1. Polish surface to be coated with #600 abrasive paper.
2. Rinse toolpiece with acetone.
4. Preheat vacuum oven to 180°C.
5. Clean spray gun with acetone.
6. Set a large spray cone (30% on N\(_2\) dial).
7. Fix a large aperture on spray gun.
8. Spray coat of KYNAR on toolpiece, holding gun at a distance of about 12 inches. Keep rotating toolpiece and continue to spray until coating just begins to appear white.
9. Immediately place toolpiece in preheated oven.
10. Bake at 180°C for 10 minutes.
11. Bake at 230°C for another 5 minutes.
12. Allow toolpiece to cool.
13. Repeat steps (4) to (12) one or two times.
14. Polish the exposed electrode surface with #600 abrasive paper to remove traces of KYNAR.
After baking the last coat, the KYNAR should appear translucent, but not brown. A brown color indicates too high a baking temperature. The final thickness of the KYNAR coating on the toolpiece was about 0.01 inch.
Appendix III: Experimental Data

Tables A1-A3 list the experimental conditions for the runs performed on the three anode materials, and Tables A4-A6 present the observed results. The parameters derived from the experimental data are shown in Tables A7-A9.
Table A1. Experimental Conditions for the ECM of TiC in 2N KNO₃:

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>\text{Em} (volts)</th>
<th>\text{Fr} (cm/min)</th>
<th>Flow Rate (lit/min)</th>
<th>Pressure (psig)</th>
<th>Specific Gravity</th>
<th>\text{t}_1 (°C)</th>
<th>\text{t}_a (°C)</th>
<th>\text{Δm} (grams)</th>
<th>\text{I}_a (amps)</th>
<th>\text{I}_f (amps)</th>
<th>Toolpiece</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11</td>
<td>14.6</td>
<td>0.0533</td>
<td>83.1</td>
<td>1.122</td>
<td>26</td>
<td>26.5</td>
<td>0.9664</td>
<td>16.7</td>
<td>17.7</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>14.7</td>
<td>0.0498</td>
<td>84.3</td>
<td>1.119</td>
<td>22</td>
<td>22.5</td>
<td>0.4373</td>
<td>16.3</td>
<td>15.8</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>9.9</td>
<td>0.0508</td>
<td>84.9</td>
<td>1.119</td>
<td>23</td>
<td>23.5</td>
<td>0.3693</td>
<td>15.1</td>
<td>15.1</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>20.2</td>
<td>0.0508</td>
<td>83.6</td>
<td>1.119</td>
<td>24</td>
<td>24.5</td>
<td>0.5307</td>
<td>19.3</td>
<td>17.8</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>15</td>
<td>14.3</td>
<td>0.0506</td>
<td>82.4</td>
<td>1.1138</td>
<td>22</td>
<td>23.0</td>
<td>1.5226</td>
<td>18.4</td>
<td>19.2</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>15</td>
<td>14.3</td>
<td>0.0510</td>
<td>81.8</td>
<td>1.1085</td>
<td>24</td>
<td>24.8</td>
<td>1.5347</td>
<td>18.3</td>
<td>19.2</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>14.4</td>
<td>0.0508</td>
<td>81.7</td>
<td>1.1085</td>
<td>25.6</td>
<td>25.7</td>
<td>0.4990</td>
<td>17.9</td>
<td>19.3</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>15</td>
<td>10.2</td>
<td>0.0271</td>
<td>82.0</td>
<td>1.1155</td>
<td>26.1</td>
<td>30.6</td>
<td>0.8484</td>
<td>10.1</td>
<td>10.8</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>10.3</td>
<td>0.0232</td>
<td>81.6</td>
<td>1.1160</td>
<td>29.3</td>
<td>32.3</td>
<td>0.7558</td>
<td>9.0</td>
<td>9.8</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>8</td>
<td>10.3</td>
<td>0.0231</td>
<td>81.6</td>
<td>1.1160</td>
<td>29.4</td>
<td>32.3</td>
<td>0.3708</td>
<td>8.5</td>
<td>10.0</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>14</td>
<td>14.6</td>
<td>0.0757</td>
<td>82.2</td>
<td>1.1165</td>
<td>29.6</td>
<td>32.9</td>
<td>2.3693</td>
<td>28.1</td>
<td>29.3</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>15</td>
<td>14.8</td>
<td>0.0543</td>
<td>81.8</td>
<td>1.1120</td>
<td>30.7</td>
<td>33.8</td>
<td>1.7609</td>
<td>21.0</td>
<td>22.1</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>15</td>
<td>14.9</td>
<td>0.0409</td>
<td>81.4</td>
<td>1.1175</td>
<td>30.6</td>
<td>33.7</td>
<td>1.3629</td>
<td>16.2</td>
<td>17.7</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>14</td>
<td>20.2</td>
<td>0.0734</td>
<td>81.9</td>
<td>1.1215</td>
<td>26.7</td>
<td>31.0</td>
<td>2.1200</td>
<td>27.0</td>
<td>28.2</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>15</td>
<td>20.3</td>
<td>0.0531</td>
<td>81.4</td>
<td>1.1210</td>
<td>29.1</td>
<td>32.7</td>
<td>1.7641</td>
<td>20.9</td>
<td>21.8</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>9</td>
<td>23.6</td>
<td>0.1113</td>
<td>82.8</td>
<td>1.1205</td>
<td>25.5</td>
<td>31.1</td>
<td>1.9895</td>
<td>39.7</td>
<td>40.8</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>2</td>
<td>23.9</td>
<td>0.1124</td>
<td>82.3</td>
<td>1.1200</td>
<td>26.7</td>
<td>30.4</td>
<td>0.3840</td>
<td>34.2</td>
<td>41.3</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>12</td>
<td>24.0</td>
<td>0.0866</td>
<td>81.3</td>
<td>1.1205</td>
<td>26.7</td>
<td>31.4</td>
<td>2.1696</td>
<td>32.5</td>
<td>33.5</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>15</td>
<td>24.0</td>
<td>0.0670</td>
<td>80.9</td>
<td>1.1205</td>
<td>28.7</td>
<td>33.2</td>
<td>2.2202</td>
<td>26.7</td>
<td>27.1</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>10</td>
<td>20.0</td>
<td>0.0981</td>
<td>82.6</td>
<td>1.1215</td>
<td>25.6</td>
<td>31.2</td>
<td>1.9252</td>
<td>34.3</td>
<td>35.4</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>15</td>
<td>20.2</td>
<td>0.0600</td>
<td>80.1</td>
<td>1.1205</td>
<td>25.4</td>
<td>28.9</td>
<td>1.9040</td>
<td>22.6</td>
<td>23.5</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>24.1</td>
<td>0.0751</td>
<td>79.2</td>
<td>1.1200</td>
<td>28.1</td>
<td>31.7</td>
<td>2.0616</td>
<td>28.2</td>
<td>29.6</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>11</td>
<td>23.9</td>
<td>0.0741</td>
<td>6.67</td>
<td>76.8</td>
<td>1.1200</td>
<td>25.6</td>
<td>28.8</td>
<td>1.7041</td>
<td>27.4</td>
<td>28.7</td>
<td>B</td>
</tr>
<tr>
<td>Run #</td>
<td>Time (min)</td>
<td>$V_{appl}$ (volts)</td>
<td>$Fr$ (cm/min)</td>
<td>Flow Rate (lit/min)</td>
<td>Pressure (psig)</td>
<td>Specific Gravity</td>
<td>$t_i$ ($^\circ$C)</td>
<td>$t_a$ ($^\circ$C)</td>
<td>$\Delta m$ (grams)</td>
<td>$I_a$ (amps)</td>
<td>$I_f$ (amps)</td>
<td>Toolpiece</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>-------------------</td>
<td>---------------</td>
<td>---------------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>22</td>
<td>15</td>
<td>14.4</td>
<td>.0515</td>
<td></td>
<td>82.1</td>
<td>1.1095</td>
<td>26.6</td>
<td>27.2</td>
<td>2.8588</td>
<td>17.0</td>
<td>17.8</td>
<td>B</td>
</tr>
<tr>
<td>27</td>
<td>2</td>
<td>14.4</td>
<td>.0502</td>
<td></td>
<td>82.8</td>
<td>1.1180</td>
<td>23.4</td>
<td>24.1</td>
<td>0.3323</td>
<td>15.3</td>
<td>16.9</td>
<td>C</td>
</tr>
<tr>
<td>45</td>
<td>15</td>
<td>14.8</td>
<td>.0531</td>
<td>1-5</td>
<td>82.3</td>
<td>1.1205</td>
<td>27.4</td>
<td>35.8</td>
<td>3.5349</td>
<td>20.0</td>
<td>22.4</td>
<td>C</td>
</tr>
<tr>
<td>46</td>
<td>9</td>
<td>20.2</td>
<td>.0945</td>
<td>4.34</td>
<td>81.7</td>
<td>1.1205</td>
<td>28.1</td>
<td>32.5</td>
<td>3.3742</td>
<td>30.2</td>
<td>31.5</td>
<td>C</td>
</tr>
<tr>
<td>47</td>
<td>8</td>
<td>24.3</td>
<td>.1142</td>
<td>4.86</td>
<td>81.0</td>
<td>1.1205</td>
<td>29.9</td>
<td>37.6</td>
<td>3.6795</td>
<td>36.4</td>
<td>37.7</td>
<td>C</td>
</tr>
<tr>
<td>48</td>
<td>15</td>
<td>10.1</td>
<td>.0292</td>
<td>0.90</td>
<td>82.9</td>
<td>1.1210</td>
<td>26.7</td>
<td>32.3</td>
<td>1.9010</td>
<td>11.4</td>
<td>12.8</td>
<td>C</td>
</tr>
<tr>
<td>72</td>
<td>3 1/2</td>
<td>10.2</td>
<td>.0256</td>
<td></td>
<td>79.8</td>
<td>1.1210</td>
<td>26.5</td>
<td>27.2</td>
<td>0.2657</td>
<td>8.5</td>
<td>10.7</td>
<td>C</td>
</tr>
<tr>
<td>73</td>
<td>5</td>
<td>10.3</td>
<td>.0204</td>
<td>2.02</td>
<td>80.5</td>
<td>1.1210</td>
<td>24.2</td>
<td>25</td>
<td>0.3913</td>
<td>8.6</td>
<td>8.9</td>
<td>C</td>
</tr>
<tr>
<td>74</td>
<td>10</td>
<td>15.1</td>
<td>.0355</td>
<td>1.92</td>
<td>1.1210</td>
<td>24.1</td>
<td>28.0</td>
<td>1.5392</td>
<td>13.7</td>
<td>13.9</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>6</td>
<td>15.0</td>
<td>.0412</td>
<td>2.24</td>
<td>1.1210</td>
<td>25.0</td>
<td>28.7</td>
<td>1.0106</td>
<td>14.2</td>
<td>14.4</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>10</td>
<td>20.3</td>
<td>.0525</td>
<td>3.94</td>
<td>1.1215</td>
<td>25.2</td>
<td>28.8</td>
<td>2.1216</td>
<td>19.1</td>
<td>19.4</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>10</td>
<td>20.1</td>
<td>.0727</td>
<td>3.11</td>
<td>1.1215</td>
<td>26.4</td>
<td>29.7</td>
<td>2.8372</td>
<td>21.5</td>
<td>22.9</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>10</td>
<td>24.3</td>
<td>.0667</td>
<td>4.58</td>
<td>1.1215</td>
<td>26.9</td>
<td>29.9</td>
<td>2.4711</td>
<td>23.8</td>
<td>24.1</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>10</td>
<td>24.3</td>
<td>.0863</td>
<td>4.76</td>
<td>1.1225</td>
<td>28.0</td>
<td>30.9</td>
<td>3.4339</td>
<td>26.4</td>
<td>27.1</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>Run</td>
<td>Time (min)</td>
<td>V applied (volts)</td>
<td>Fr (cm³/min)</td>
<td>P Pressure (psi)</td>
<td>S* (wt%)</td>
<td>Flow Rate (lit/min)</td>
<td>e (°C)</td>
<td>t₀ (°C)</td>
<td>am (grams)</td>
<td>I₀ (amps)</td>
<td>I_f (amps)</td>
<td>Tool-piece</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>------------------</td>
<td>--------------</td>
<td>-----------------</td>
<td>-----------</td>
<td>---------------------</td>
<td>--------</td>
<td>---------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>21</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>22</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>23</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>24</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>25</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>26</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>27</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>28</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>29</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
<tr>
<td>30</td>
<td>2 1/2</td>
<td>14.5</td>
<td>6.17</td>
<td>79.7</td>
<td>1.1165</td>
<td>21.9</td>
<td>27.2</td>
<td>28.5</td>
<td>30.4</td>
<td>14.9</td>
<td>19.6</td>
<td>B</td>
</tr>
</tbody>
</table>

Table A3. Experimental Conditions for the ECM of TIC/Ni in 2N KOH.
Table A4. Experimental Results from the ECM of TiC in 2N KNO₃.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Time (min)</th>
<th>V_appl. (volts)</th>
<th>F_r (cm/min)</th>
<th>S_g (mils)</th>
<th>h (mils)</th>
<th>Δ (mils)</th>
<th>ε (mils)</th>
<th>d* (cm)</th>
<th>a (cm²)</th>
<th>i_a (A/cm²)</th>
<th>i_f (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11</td>
<td>14.6</td>
<td>.0533</td>
<td>30.0</td>
<td>219</td>
<td>231</td>
<td>18</td>
<td>.750</td>
<td>.4418</td>
<td>37.8</td>
<td>40.1</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>14.7</td>
<td>.0498</td>
<td>6.0</td>
<td>109</td>
<td>98</td>
<td>17</td>
<td>.720</td>
<td>.4072</td>
<td>40.0</td>
<td>38.8</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>9.9</td>
<td>.0508</td>
<td>6.0</td>
<td>107.5</td>
<td>100</td>
<td>13.5</td>
<td>.690</td>
<td>.3739</td>
<td>40.3</td>
<td>40.4</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>20.2</td>
<td>.0508</td>
<td>6.0</td>
<td>120</td>
<td>100</td>
<td>26</td>
<td>.750</td>
<td>.4418</td>
<td>43.6</td>
<td>40.3</td>
</tr>
<tr>
<td>18</td>
<td>15</td>
<td>14.3</td>
<td>.0506</td>
<td>20.0</td>
<td>297</td>
<td>301</td>
<td>17</td>
<td>.735</td>
<td>.4243</td>
<td>43.2</td>
<td>45.3</td>
</tr>
<tr>
<td>19</td>
<td>15</td>
<td>14.3</td>
<td>.0510</td>
<td>20.0</td>
<td>98</td>
<td>100</td>
<td>18</td>
<td>.740</td>
<td>.4301</td>
<td>41.7</td>
<td>44.9</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>14.4</td>
<td>.0508</td>
<td>20.0</td>
<td>153</td>
<td>160.0</td>
<td>18</td>
<td>.760</td>
<td>.4536</td>
<td>22.3</td>
<td>23.8</td>
</tr>
<tr>
<td>29</td>
<td>15</td>
<td>10.2</td>
<td>.0271</td>
<td>25.0</td>
<td>153</td>
<td>160.0</td>
<td>18</td>
<td>.760</td>
<td>.4536</td>
<td>22.3</td>
<td>23.8</td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>10.3</td>
<td>.0232</td>
<td>25.0</td>
<td>135</td>
<td>137.2</td>
<td>22.8</td>
<td>.780</td>
<td>.4778</td>
<td>18.9</td>
<td>20.5</td>
</tr>
<tr>
<td>31</td>
<td>8</td>
<td>10.3</td>
<td>.0231</td>
<td>25.0</td>
<td>71</td>
<td>72.7</td>
<td>23.3</td>
<td>.785</td>
<td>.4840</td>
<td>17.6</td>
<td>20.7</td>
</tr>
<tr>
<td>32</td>
<td>15</td>
<td>14.6</td>
<td>.0757</td>
<td>25.0</td>
<td>434</td>
<td>446.1</td>
<td>12.9</td>
<td>.750</td>
<td>.4418</td>
<td>63.7</td>
<td>66.3</td>
</tr>
<tr>
<td>33</td>
<td>15</td>
<td>14.8</td>
<td>.0543</td>
<td>25.0</td>
<td>313</td>
<td>320.4</td>
<td>17.6</td>
<td>.775</td>
<td>.4717</td>
<td>44.5</td>
<td>46.9</td>
</tr>
<tr>
<td>34</td>
<td>15</td>
<td>14.9</td>
<td>.0409</td>
<td>25.0</td>
<td>239</td>
<td>241.3</td>
<td>22.7</td>
<td>.785</td>
<td>.4840</td>
<td>33.5</td>
<td>36.6</td>
</tr>
<tr>
<td>36</td>
<td>14</td>
<td>20.2</td>
<td>.0734</td>
<td>25.0</td>
<td>399</td>
<td>404.6</td>
<td>19.4</td>
<td>.745</td>
<td>.4359</td>
<td>61.9</td>
<td>64.7</td>
</tr>
<tr>
<td>37</td>
<td>15</td>
<td>20.3</td>
<td>.0531</td>
<td>25.0</td>
<td>315</td>
<td>313.5</td>
<td>26.5</td>
<td>.770</td>
<td>.4657</td>
<td>45.0</td>
<td>46.8</td>
</tr>
<tr>
<td>38</td>
<td>9</td>
<td>23.6</td>
<td>.1113</td>
<td>25.0</td>
<td>388</td>
<td>394.4</td>
<td>18.6</td>
<td>.750</td>
<td>.4418</td>
<td>97.5</td>
<td>92.4</td>
</tr>
<tr>
<td>39</td>
<td>2</td>
<td>23.9</td>
<td>.1124</td>
<td>25.0</td>
<td>78</td>
<td>88.5</td>
<td>14.5</td>
<td>.725</td>
<td>.4128</td>
<td>82.9</td>
<td>100.1</td>
</tr>
<tr>
<td>40</td>
<td>12</td>
<td>24.0</td>
<td>.0666</td>
<td>25.0</td>
<td>405</td>
<td>409.2</td>
<td>20.8</td>
<td>.750</td>
<td>.4418</td>
<td>73.5</td>
<td>75.8</td>
</tr>
<tr>
<td>41</td>
<td>15</td>
<td>24.0</td>
<td>.0670</td>
<td>25.0</td>
<td>398</td>
<td>395.7</td>
<td>27.3</td>
<td>.755</td>
<td>.4477</td>
<td>59.6</td>
<td>60.5</td>
</tr>
<tr>
<td>43</td>
<td>10</td>
<td>20.0</td>
<td>.0981</td>
<td>25.0</td>
<td>379</td>
<td>386.2</td>
<td>17.8</td>
<td>.750</td>
<td>.4418</td>
<td>83.1</td>
<td>80.1</td>
</tr>
<tr>
<td>49</td>
<td>15</td>
<td>20.2</td>
<td>.0600</td>
<td>25.0</td>
<td>352</td>
<td>354.1</td>
<td>22.9</td>
<td>.750</td>
<td>.4418</td>
<td>51.2</td>
<td>53.2</td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>24.1</td>
<td>.0751</td>
<td>25.0</td>
<td>378</td>
<td>384.5</td>
<td>18.5</td>
<td>.750</td>
<td>.4418</td>
<td>63.7</td>
<td>67.0</td>
</tr>
<tr>
<td>57</td>
<td>11</td>
<td>23.9</td>
<td>.0741</td>
<td>25.0</td>
<td>318</td>
<td>320.9</td>
<td>22.1</td>
<td>.750</td>
<td>.4418</td>
<td>62.1</td>
<td>65.0</td>
</tr>
</tbody>
</table>

* Toolpiece diameter = 0.666 - 0.671 cm (see Table 2).
<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>$V_{applied}$ (volts)</th>
<th>$F_r$ (cm/min)</th>
<th>$d$ (cm)</th>
<th>$d^2$ (cm$^2$)</th>
<th>$i$ (mA)</th>
<th>$i^2$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>15</td>
<td>14.4</td>
<td>0.00</td>
<td>20.0</td>
<td>300.1</td>
<td>24</td>
<td>41.80</td>
</tr>
<tr>
<td>27</td>
<td>12</td>
<td>14.4</td>
<td>0.00</td>
<td>20.0</td>
<td>39.5</td>
<td>21</td>
<td>40.7</td>
</tr>
<tr>
<td>45</td>
<td>9</td>
<td>14.8</td>
<td>0.00</td>
<td>25.0</td>
<td>321</td>
<td>21</td>
<td>35.9</td>
</tr>
<tr>
<td>46</td>
<td>9</td>
<td>20.2</td>
<td>0.000</td>
<td>25.0</td>
<td>331</td>
<td>22.7</td>
<td>43.1</td>
</tr>
<tr>
<td>47</td>
<td>8</td>
<td>24.3</td>
<td>0.000</td>
<td>25.0</td>
<td>335</td>
<td>23.0</td>
<td>68.1</td>
</tr>
<tr>
<td>48</td>
<td>3 1/2</td>
<td>10.1</td>
<td>0.000</td>
<td>25.0</td>
<td>335</td>
<td>23.3</td>
<td>80.3</td>
</tr>
<tr>
<td>72</td>
<td>5</td>
<td>10.3</td>
<td>0.000</td>
<td>25.0</td>
<td>335</td>
<td>23.3</td>
<td>80.3</td>
</tr>
<tr>
<td>73</td>
<td>5</td>
<td>10.3</td>
<td>0.000</td>
<td>25.0</td>
<td>335</td>
<td>23.3</td>
<td>80.3</td>
</tr>
<tr>
<td>74</td>
<td>10</td>
<td>15.1</td>
<td>0.000</td>
<td>25.0</td>
<td>356</td>
<td>33.8</td>
<td>17.9</td>
</tr>
<tr>
<td>75</td>
<td>6</td>
<td>15.0</td>
<td>0.000</td>
<td>25.0</td>
<td>356</td>
<td>33.8</td>
<td>17.9</td>
</tr>
<tr>
<td>76</td>
<td>10</td>
<td>20.3</td>
<td>0.000</td>
<td>25.0</td>
<td>356</td>
<td>33.8</td>
<td>17.9</td>
</tr>
<tr>
<td>77</td>
<td>10</td>
<td>20.3</td>
<td>0.000</td>
<td>25.0</td>
<td>356</td>
<td>33.8</td>
<td>17.9</td>
</tr>
<tr>
<td>78</td>
<td>10</td>
<td>20.3</td>
<td>0.000</td>
<td>25.0</td>
<td>356</td>
<td>33.8</td>
<td>17.9</td>
</tr>
<tr>
<td>79</td>
<td>10</td>
<td>20.3</td>
<td>0.000</td>
<td>25.0</td>
<td>356</td>
<td>33.8</td>
<td>17.9</td>
</tr>
</tbody>
</table>

**Toolpiece diameter = 0.666 - 0.671 cm (see Table 2).**
### Table A6. Experimental Results from the ECM of TiC/Ni in 2N KNO₃

<table>
<thead>
<tr>
<th>Run #</th>
<th>Time (min)</th>
<th>V&lt;sub&gt;appl&lt;/sub&gt; (volts)</th>
<th>Fr (cm/min)</th>
<th>SG (mils)</th>
<th>h (mils)</th>
<th>δ (mils)</th>
<th>t (mils)</th>
<th>a (cm)</th>
<th>a&lt;sup&gt;*&lt;/sup&gt; (cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>i&lt;sub&gt;a&lt;/sub&gt; (A/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>i&lt;sub&gt;f&lt;/sub&gt; (A/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>15</td>
<td>14.4</td>
<td>.0511</td>
<td>20.0</td>
<td>297</td>
<td>302</td>
<td>15</td>
<td>.745</td>
<td>.4359</td>
<td>40.6</td>
<td>45.0</td>
</tr>
<tr>
<td>23</td>
<td>3</td>
<td>14.4</td>
<td>.0500</td>
<td>20.0</td>
<td>57.5</td>
<td>59</td>
<td>18.5</td>
<td>.750</td>
<td>.4418</td>
<td>33.8</td>
<td>40.7</td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>14.4</td>
<td>.0502</td>
<td>20.0</td>
<td>33</td>
<td>39.5</td>
<td>13.5</td>
<td>.740</td>
<td>.4301</td>
<td>36.0</td>
<td>51.6</td>
</tr>
<tr>
<td>25</td>
<td>2 1/2</td>
<td>14.5</td>
<td>.0493</td>
<td>20.0</td>
<td>42.5</td>
<td>48.5</td>
<td>14</td>
<td>.750</td>
<td>.4418</td>
<td>38.0</td>
<td>50.0</td>
</tr>
<tr>
<td>26</td>
<td>2 1/2</td>
<td>14.5</td>
<td>.0498</td>
<td>20.0</td>
<td>41.5</td>
<td>49</td>
<td>12.5</td>
<td>.735</td>
<td>.4243</td>
<td>37.1</td>
<td>47.8</td>
</tr>
<tr>
<td>54</td>
<td>8</td>
<td>10.2</td>
<td>.0229</td>
<td>25.0</td>
<td>68</td>
<td>72.1</td>
<td>20.9</td>
<td>.750</td>
<td>.4418</td>
<td>18.4</td>
<td>21.3</td>
</tr>
<tr>
<td>55</td>
<td>1 1/2</td>
<td>24.0</td>
<td>.1085</td>
<td>25.0</td>
<td>49</td>
<td>64.1</td>
<td>9.9</td>
<td>.730</td>
<td>.4185</td>
<td>72.6</td>
<td>95.3</td>
</tr>
<tr>
<td>56</td>
<td>2</td>
<td>19.9</td>
<td>.0918</td>
<td>25.0</td>
<td>59</td>
<td>72.3</td>
<td>11.7</td>
<td>.730</td>
<td>.4185</td>
<td>58.8</td>
<td>74.1</td>
</tr>
<tr>
<td>58</td>
<td>15</td>
<td>10.2</td>
<td>.0205</td>
<td>25.0</td>
<td>116</td>
<td>121.0</td>
<td>20.0</td>
<td>.755</td>
<td>.4477</td>
<td>18.8</td>
<td>21.0</td>
</tr>
<tr>
<td>59</td>
<td>8</td>
<td>24.3</td>
<td>.0665</td>
<td>25.0</td>
<td>207</td>
<td>209.3</td>
<td>22.7</td>
<td>.760</td>
<td>.4536</td>
<td>58.1</td>
<td>60.4</td>
</tr>
<tr>
<td>61</td>
<td>15</td>
<td>10.2</td>
<td>.0214</td>
<td>25.0</td>
<td>131</td>
<td>126.3</td>
<td>29.7</td>
<td>.740</td>
<td>.4301</td>
<td>20.7</td>
<td>19.8</td>
</tr>
<tr>
<td>62</td>
<td>9</td>
<td>10.0</td>
<td>.0345</td>
<td>25.0</td>
<td>120</td>
<td>122.1</td>
<td>22.9</td>
<td>.710</td>
<td>.3959</td>
<td>31.6</td>
<td>34.9</td>
</tr>
<tr>
<td>63</td>
<td>10</td>
<td>15.0</td>
<td>.0344</td>
<td>25.0</td>
<td>141</td>
<td>135.4</td>
<td>30.6</td>
<td>.755</td>
<td>.4477</td>
<td>27.7</td>
<td>29.0</td>
</tr>
<tr>
<td>65</td>
<td>10</td>
<td>20.3</td>
<td>.0511</td>
<td>25.0</td>
<td>206</td>
<td>201.2</td>
<td>29.8</td>
<td>.750</td>
<td>.4418</td>
<td>41.2</td>
<td>43.7</td>
</tr>
<tr>
<td>66</td>
<td>2</td>
<td>19.8</td>
<td>.0921</td>
<td>25.0</td>
<td>62</td>
<td>72.5</td>
<td>14.5</td>
<td>.715</td>
<td>.4015</td>
<td>68.5</td>
<td>88.2</td>
</tr>
<tr>
<td>67</td>
<td>8</td>
<td>24.4</td>
<td>.0661</td>
<td>25.0</td>
<td>211</td>
<td>208.3</td>
<td>27.7</td>
<td>.760</td>
<td>.4536</td>
<td>51.5</td>
<td>58.0</td>
</tr>
<tr>
<td>68</td>
<td>6</td>
<td>24.1</td>
<td>.0839</td>
<td>25.0</td>
<td>198</td>
<td>198.3</td>
<td>24.7</td>
<td>.730</td>
<td>.4185</td>
<td>83.7</td>
<td>96.1</td>
</tr>
<tr>
<td>69</td>
<td>10</td>
<td>14.7</td>
<td>.0370</td>
<td>25.0</td>
<td>145</td>
<td>145.6</td>
<td>24.4</td>
<td>.750</td>
<td>.4418</td>
<td>35.8</td>
<td>39.8</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
<td>19.9</td>
<td>.0722</td>
<td>25.0</td>
<td>129</td>
<td>142.2</td>
<td>11.8</td>
<td>.735</td>
<td>.4243</td>
<td>54.3</td>
<td>64.6</td>
</tr>
<tr>
<td>71</td>
<td>3</td>
<td>24.1</td>
<td>.0758</td>
<td>25.0</td>
<td>80</td>
<td>89.5</td>
<td>15.5</td>
<td>.740</td>
<td>.4301</td>
<td>60.1</td>
<td>71.8</td>
</tr>
</tbody>
</table>

Toolpiece diameter = 0.666 - 0.671 cm (see Table 2).
Table A7. Derived Parameters from the Experimental Data for the ECM of TiC in 2N KN0₃.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Time (min)</th>
<th>V_{appl.} (volts)</th>
<th>Fr (cm/min)</th>
<th>k (\Omega^{-1} \text{cm}^{-1})</th>
<th>V_{fr} (volts)</th>
<th>n (eq.gmol)</th>
<th>z (Vmin/\text{cm}²)</th>
<th>d.f.</th>
<th>m (g/min)</th>
<th>Ṽ (cm³/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11</td>
<td>14.6</td>
<td>0.0533</td>
<td>0.1766</td>
<td>10.4</td>
<td>+4.2</td>
<td>7.07</td>
<td>34.36</td>
<td>0.0879</td>
<td>0.0200</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>14.7</td>
<td>0.0498</td>
<td>0.1552</td>
<td>10.8</td>
<td>+3.9</td>
<td>6.93</td>
<td>33.66</td>
<td>0.0875</td>
<td>0.0199</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>9.9</td>
<td>0.0508</td>
<td>0.1596</td>
<td>8.7</td>
<td>+1.2</td>
<td>7.60</td>
<td>27.27</td>
<td>0.0739</td>
<td>0.0168</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>20.2</td>
<td>0.0508</td>
<td>0.1641</td>
<td>16.2</td>
<td>+4.0</td>
<td>6.76</td>
<td>52.36</td>
<td>0.1061</td>
<td>0.0241</td>
</tr>
<tr>
<td>18</td>
<td>15</td>
<td>14.3</td>
<td>0.0506</td>
<td>0.1520</td>
<td>13.4</td>
<td>+0.9</td>
<td>6.73</td>
<td>40.34</td>
<td>0.1015</td>
<td>0.0231</td>
</tr>
<tr>
<td>19</td>
<td>15</td>
<td>14.3</td>
<td>0.0510</td>
<td>0.1546</td>
<td>12.6</td>
<td>+1.7</td>
<td>6.67</td>
<td>38.32</td>
<td>0.1023</td>
<td>0.0233</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>14.4</td>
<td>0.0518</td>
<td>0.1588</td>
<td>12.9</td>
<td>+1.5</td>
<td>6.69</td>
<td>40.39</td>
<td>0.0998</td>
<td>0.0227</td>
</tr>
<tr>
<td>29</td>
<td>15</td>
<td>10.2</td>
<td>0.0271</td>
<td>0.1881</td>
<td>5.8</td>
<td>+4.4</td>
<td>6.67</td>
<td>40.19</td>
<td>0.0566</td>
<td>0.0129</td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>10.3</td>
<td>0.0232</td>
<td>0.1986</td>
<td>6.0</td>
<td>+4.3</td>
<td>6.68</td>
<td>51.19</td>
<td>0.0504</td>
<td>0.0115</td>
</tr>
<tr>
<td>31</td>
<td>8</td>
<td>10.3</td>
<td>0.0231</td>
<td>0.1987</td>
<td>6.2</td>
<td>+4.1</td>
<td>6.84</td>
<td>52.90</td>
<td>0.0464</td>
<td>0.0105</td>
</tr>
<tr>
<td>32</td>
<td>14, 58, 60</td>
<td>14.6</td>
<td>0.0757</td>
<td>0.2024</td>
<td>10.7</td>
<td>+3.9</td>
<td>6.62</td>
<td>28.72</td>
<td>0.1583</td>
<td>0.0360</td>
</tr>
<tr>
<td>33</td>
<td>15</td>
<td>14.8</td>
<td>0.0543</td>
<td>0.2019</td>
<td>10.4</td>
<td>+4.4</td>
<td>6.66</td>
<td>38.56</td>
<td>0.1174</td>
<td>0.0267</td>
</tr>
<tr>
<td>34</td>
<td>15</td>
<td>14.9</td>
<td>0.0409</td>
<td>0.2084</td>
<td>10.1</td>
<td>+4.8</td>
<td>6.64</td>
<td>51.56</td>
<td>0.0909</td>
<td>0.0207</td>
</tr>
<tr>
<td>36</td>
<td>14</td>
<td>20.2</td>
<td>0.0734</td>
<td>0.1974</td>
<td>16.2</td>
<td>+4.0</td>
<td>6.63</td>
<td>43.43</td>
<td>0.1514</td>
<td>0.0344</td>
</tr>
<tr>
<td>37</td>
<td>15</td>
<td>20.3</td>
<td>0.0531</td>
<td>0.2067</td>
<td>15.2</td>
<td>+5.1</td>
<td>6.63</td>
<td>59.32</td>
<td>0.1176</td>
<td>0.0267</td>
</tr>
<tr>
<td>38</td>
<td>9</td>
<td>23.6</td>
<td>0.1113</td>
<td>0.1961</td>
<td>22.3</td>
<td>+1.3</td>
<td>6.69</td>
<td>39.20</td>
<td>0.2211</td>
<td>0.0503</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>23.9</td>
<td>0.1124</td>
<td>0.1927</td>
<td>19.1</td>
<td>+4.8</td>
<td>6.64</td>
<td>32.78</td>
<td>0.1920</td>
<td>0.0436</td>
</tr>
<tr>
<td>40</td>
<td>12</td>
<td>24.0</td>
<td>0.0866</td>
<td>0.1982</td>
<td>20.2</td>
<td>+3.8</td>
<td>6.69</td>
<td>46.25</td>
<td>0.1808</td>
<td>0.0411</td>
</tr>
<tr>
<td>41</td>
<td>15</td>
<td>24.0</td>
<td>0.0670</td>
<td>0.2085</td>
<td>20.1</td>
<td>+3.9</td>
<td>6.71</td>
<td>62.64</td>
<td>0.1480</td>
<td>0.0336</td>
</tr>
<tr>
<td>43</td>
<td>10</td>
<td>20.0</td>
<td>0.0981</td>
<td>0.1978</td>
<td>18.3</td>
<td>+1.7</td>
<td>6.64</td>
<td>36.94</td>
<td>0.1925</td>
<td>0.0438</td>
</tr>
<tr>
<td>49</td>
<td>15</td>
<td>20.2</td>
<td>0.0600</td>
<td>0.1856</td>
<td>16.7</td>
<td>+3.5</td>
<td>6.64</td>
<td>51.57</td>
<td>0.1269</td>
<td>0.0288</td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>24.1</td>
<td>0.0751</td>
<td>0.1999</td>
<td>15.8</td>
<td>+8.3</td>
<td>6.61</td>
<td>41.92</td>
<td>0.1586</td>
<td>0.0360</td>
</tr>
<tr>
<td>57</td>
<td>11</td>
<td>23.9</td>
<td>0.0741</td>
<td>0.1846</td>
<td>19.8</td>
<td>+4.1</td>
<td>6.59</td>
<td>49.20</td>
<td>0.1549</td>
<td>0.0352</td>
</tr>
<tr>
<td>Run #</td>
<td>Time (min)</td>
<td>( V_{\text{appl.}} ) (volts)</td>
<td>( k ) (cm/min)</td>
<td>( F_r ) (cm/min)</td>
<td>( z )</td>
<td>( \dot{m} ) (g/min)</td>
<td>( \dot{V}_{\text{vol.}} ) (cm³/min)</td>
<td>( \text{d.f.} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----</td>
<td>-----------------</td>
<td>-----------------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>15</td>
<td>14.4</td>
<td>-0.0315</td>
<td>0.0501</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>2</td>
<td>14.4</td>
<td>0.0501</td>
<td>0.0531</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>10</td>
<td>15.9</td>
<td>0.0531</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>9.7</td>
<td>20.2</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>9.7</td>
<td>24.3</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>10.1</td>
<td>11.1</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>10.1</td>
<td>24.3</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>10.1</td>
<td>10.2</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>10.1</td>
<td>15.1</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>10.1</td>
<td>15.0</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>10.1</td>
<td>20.3</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>10.1</td>
<td>24.3</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>10.1</td>
<td>24.3</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>10.1</td>
<td>24.3</td>
<td>0.0945</td>
<td>0.0945</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A8. Derived parameters from the Experimental Data for the ECH of Ni 200 in 2N KNO₃.
Table A9. Derived Parameters from the Experimental Data for the ECM of TiC/Ni in 2N KNO₃.

<table>
<thead>
<tr>
<th>Run</th>
<th>Time</th>
<th>V&lt;sub&gt;appl&lt;/sub&gt;</th>
<th>Fr</th>
<th>k</th>
<th>V&lt;sub&gt;ir&lt;/sub&gt;</th>
<th>n</th>
<th>z</th>
<th>d.f.</th>
<th>m</th>
<th>V&lt;sub&gt;Vol&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>15</td>
<td>14.4</td>
<td>.0511</td>
<td>.1619</td>
<td>10.6</td>
<td>+3.8</td>
<td>6.80</td>
<td>33.58</td>
<td>.0967</td>
<td>.0201</td>
</tr>
<tr>
<td>23</td>
<td>3</td>
<td>14.4</td>
<td>.0500</td>
<td>.1584</td>
<td>12.1</td>
<td>+2.3</td>
<td>7.40</td>
<td>38.33</td>
<td>.0751</td>
<td>.0156</td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>14.4</td>
<td>.0502</td>
<td>.1609</td>
<td>11.0</td>
<td>+3.4</td>
<td>6.90</td>
<td>35.26</td>
<td>.0836</td>
<td>.0174</td>
</tr>
<tr>
<td>25</td>
<td>2 1/2</td>
<td>14.5</td>
<td>.0493</td>
<td>.1507</td>
<td>11.8</td>
<td>+2.7</td>
<td>7.12</td>
<td>36.07</td>
<td>.0876</td>
<td>.0183</td>
</tr>
<tr>
<td>26</td>
<td>2 1/2</td>
<td>14.5</td>
<td>.0498</td>
<td>.1516</td>
<td>10.0</td>
<td>+4.5</td>
<td>6.75</td>
<td>30.44</td>
<td>.0868</td>
<td>.0181</td>
</tr>
<tr>
<td>54</td>
<td>8</td>
<td>10.2</td>
<td>.0229</td>
<td>.1769</td>
<td>6.4</td>
<td>+3.8</td>
<td>6.64</td>
<td>49.44</td>
<td>.0455</td>
<td>.0095</td>
</tr>
<tr>
<td>55</td>
<td>1 1/2</td>
<td>24.0</td>
<td>.1085</td>
<td>.1828</td>
<td>13.1</td>
<td>+10.9</td>
<td>6.46</td>
<td>22.07</td>
<td>.1747</td>
<td>.0364</td>
</tr>
<tr>
<td>56</td>
<td>2</td>
<td>19.9</td>
<td>.0918</td>
<td>.1833</td>
<td>12.0</td>
<td>+7.9</td>
<td>5.87</td>
<td>23.96</td>
<td>.1558</td>
<td>.0325</td>
</tr>
<tr>
<td>58</td>
<td>15</td>
<td>10.2</td>
<td>.0205</td>
<td>.1873</td>
<td>5.7</td>
<td>+4.5</td>
<td>5.20</td>
<td>52.08</td>
<td>.0602</td>
<td>.0125</td>
</tr>
<tr>
<td>59</td>
<td>6</td>
<td>24.3</td>
<td>.0665</td>
<td>.1983</td>
<td>17.6</td>
<td>+6.7</td>
<td>7.58</td>
<td>52.48</td>
<td>.1293</td>
<td>.0269</td>
</tr>
<tr>
<td>61</td>
<td>15</td>
<td>10.2</td>
<td>.0214</td>
<td>.1879</td>
<td>7.9</td>
<td>+2.3</td>
<td>6.94</td>
<td>69.36</td>
<td>.0478</td>
<td>.0100</td>
</tr>
<tr>
<td>62</td>
<td>9</td>
<td>10.0</td>
<td>.0345</td>
<td>.1977</td>
<td>10.3</td>
<td>-0.3</td>
<td>6.61</td>
<td>59.02</td>
<td>.0704</td>
<td>.0147</td>
</tr>
<tr>
<td>63</td>
<td>10</td>
<td>15.0</td>
<td>.0344</td>
<td>.1711</td>
<td>13.2</td>
<td>+1.8</td>
<td>6.72</td>
<td>65.65</td>
<td>.0685</td>
<td>.0143</td>
</tr>
<tr>
<td>65</td>
<td>10</td>
<td>20.3</td>
<td>.0511</td>
<td>.1811</td>
<td>18.3</td>
<td>+2.0</td>
<td>6.40</td>
<td>64.86</td>
<td>.1057</td>
<td>.0220</td>
</tr>
<tr>
<td>66</td>
<td>2</td>
<td>19.8</td>
<td>.0921</td>
<td>.1850</td>
<td>17.6</td>
<td>+2.2</td>
<td>6.59</td>
<td>35.35</td>
<td>.1551</td>
<td>.0323</td>
</tr>
<tr>
<td>67</td>
<td>8</td>
<td>24.4</td>
<td>.0661</td>
<td>.1873</td>
<td>21.8</td>
<td>+2.6</td>
<td>6.40</td>
<td>61.77</td>
<td>.1357</td>
<td>.0283</td>
</tr>
<tr>
<td>68</td>
<td>6</td>
<td>24.1</td>
<td>.0839</td>
<td>.2044</td>
<td>29.5</td>
<td>-5.4</td>
<td>6.80</td>
<td>71.87</td>
<td>.1916</td>
<td>.0399</td>
</tr>
<tr>
<td>69</td>
<td>10</td>
<td>14.7</td>
<td>.0370</td>
<td>.1853</td>
<td>13.3</td>
<td>+1.4</td>
<td>7.65</td>
<td>66.61</td>
<td>.0796</td>
<td>.0160</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
<td>19.9</td>
<td>.0722</td>
<td>.1906</td>
<td>10.2</td>
<td>+9.7</td>
<td>6.74</td>
<td>26.93</td>
<td>.1270</td>
<td>.0265</td>
</tr>
<tr>
<td>71</td>
<td>3</td>
<td>24.1</td>
<td>.0758</td>
<td>.1887</td>
<td>15.0</td>
<td>+9.1</td>
<td>6.92</td>
<td>37.34</td>
<td>.1388</td>
<td>.0289</td>
</tr>
</tbody>
</table>
Appendix IV: Additional Experimental Observations

Several unusual phenomena were observed in the ECM of Ni 200. In all of the experimental runs, a sharp lip was observed at the top of each hole. The diameter of the hole at the lip was, on the average, 0.04 cm smaller than the diameter of the rest of the hole. Note that the larger diameter is the one reported in the tables of data in Appendix III.

Figure A2a shows the result of a 45-second ECM run done on Ni 200 at 10 volts applied voltage and a toolpiece feed rate of 0.03 cm/min. This run exhibits the flow pattern of the electrolyte and the initial shaping of the workpiece, before the cathode tool has penetrated the toolpiece.

Figure A2b is a schematic diagram of the indentation, which is square-shaped with four spikes coming out of the sides of the square. The small circles (A) represent low humps that are discernible on the surface; these humps correspond to the location of the five electrolyte exit holes in the toolpiece. The diameter of the toolpiece is represented by circle (B) in the diagram.

The spiked indentations probably result from the junction of electrolyte flows from neighboring toolpiece holes. If the run had been continued, the final diameter of the hole would have been approximately equal to that of circle (C) in Fig. A2b.

In some of the experimental runs performed at low applied voltage/low toolpiece feed rate, the post-ECM nickel surface exhibited a shiny region of a specific pattern. An example is shown in Fig. A3. One observes a dark, x-shaped region over most of the surface at the bottom of the hole; around the x-shape, the nickel is shiny. This pattern
Fig. A2. Ni 200 surface after a 45-second ECM run (Machining conditions: \( V = 10 \) volts, \( F_s = 0.03 \) cm/min).
(a) Photograph of Ni 200 surface (6.5X magnification).
(b) Schematic diagram of indentation.
Fig. A3. (a) Ni 200 anode with post-ECM run exhibiting shiny pattern (2.8X magnification).
(b) Closeup of shiny run (6.6X magnification). (Machining conditions: $V = 10$ volts, 
Fr = 0.03 cm/min).
suggests that the non-shiny region corresponds to the electrolyte exit holes in the toolpiece, where the flow is fastest, while the shiny areas correspond to the flow regions between the toolpiece holes, where the electrolyte flow is slower.
References

   Presented at the 1940 and 1941 Conferences on Powder Metallurgy Held
   at the Massachusetts Institute of Technology, Cambridge, John Wulff,

2. S. W. H. Yih and C. T. Wang, Tungsten: Sources, Metallurgy,

3. C. J. Smithells, Tungsten: Its Metallurgy, Properties and Applications

4. K. C. Li and C. Y. Wang, Tungsten: Its History, Geology, Ore-Dressing,
   Metallurgy, Chemistry, Analysis, Applications, and Economics (New York:

5. M. B. Waldron and B. L. Daniell, Sintering (Philadelphia: Heyden,
   1978).

   by the Pennsalt Chemicals Corporation, Philadelphia, Pennsylvania,
   1967.
List of Symbols

a = cross-sectional area of ECM hole (cm²)
b = electrolyte constant, equation (18)
C_i = concentration of ions at interfaces (gmol/lit)
C_b = concentration of ions in bulk solution (gmol/lit)
CE = current efficiency of dissolution
d = diameter of ECM hole (cm)
d.f. = ECM driving force = k V_i/Vi (V min/Ω cm²)
E_0 = thermodynamic equilibrium potential (V)
F = Faraday's constant = 96,500 C/eq
Fr = toolpiece feed rate (cm/min)
h = depth of ECM hole (mils, cm)
I = current (A)
I_a = average current of run (A)
I_f = final current of run (A)
i = current density (A/cm²)
i_a = average current density of run (A/cm²)
i_f = final current density of run (A/cm²)
k = electrolyte conductivity (Ω⁻¹ cm⁻¹)
k_0 = electrolyte conductivity at reference temperature (Ω⁻¹ cm⁻¹)
k_20 = electrolyte conductivity at a reference temperature of 20°C (Ω⁻¹ cm⁻¹)
ε = interelectrode gap (mils, cm)
m = mass (g)
Δm = mass loss (g)
ṁ = mass removal rate (g/min)
M = molecular weight (g/gmol)
\( M \) = weighted molecular weight (g/gmol)  
\( n \) = electrochemical valence of discharged ion  
\( P \) = pressure (psig)  
\( Q \) = flow rate of electrolyte (lit/min)  
\( R \) = resistance (\( \Omega \))  
\( S \) = specific gravity of electrolyte  
\( S_G \) = ECM starting gap (mils, cm)  
\( t \) = time (min, sec)  
\( t \) = temperature (\( ^\circ C \)), equation (18)  
\( t_a \) = average temperature of electrolyte during run (\( ^\circ C \))  
\( t_i \) = initial temperature of electrolyte (\( ^\circ C \))  
\( t_o \) = reference temperature (\( ^\circ C \))  
\( V \) = applied voltage (V)  
\( V_{ir} \) = ohmic drop through electrolyte (V)  
\( V_{\text{Vol}} \) = volume loss (cm\(^3\))  
\( V_{\text{Vol}} \) = volume removal rate (cm\(^3\)/min)  
\( z \) = valence of dissolution (eq/gmol)  
\( z_{\text{app}} \) = apparent valence of dissolution (eq/gmol)  
\( \bar{z} \) = average valence of dissolution (eq/gmol)  
\( \alpha \) = system parameter = \( \frac{M}{F Z \rho} \) (cm\(^3\)/C)  
\( \beta \) = constant, equation (13)  
\( \eta \) = sum of thermodynamic equilibrium potential and overvoltages = \( E_o + \eta_a + \eta_c + \eta_r \) (V)  
\( \bar{\eta} \) = average value for \( \eta \) (V)
\( \eta_a \) = activation overvoltage (V)
\( \eta_c \) = concentration overvoltage (V)
\( \eta_r \) = resistance overvoltage (V)
\( \rho \) = density (g/cm\(^3\))
\( \rho' \) = resistivity (\( \Omega \)cm)
\( \rho_{\text{lit.}} \) = density of pore-free material reported in the literature (g/cm\(^3\))
\( \rho_{\text{obs.}} \) = observed density (g/cm\(^3\))
\( \tau \) = time (min)
Acknowledgment

I would like to express my gratitude to Professor Tobias and to Dr. Muller for their generous support and critical evaluation during the course of this study.

I am also indebted to Professor Pask for the review of this manuscript.

For invaluable technical assistance with the project, I would like to thank Ken Gaugler and John Holthuis, as well as Kennametal Inc.

My special thanks go to Gay Brazil for typing this manuscript, and to Gloria Pelatowski for assistance with the figures.

Finally, I would like to thank the many friends and fellow graduate students who gave their support and assistance in this project, in particular Dennis Dees, Shannon O'Grady, Toula Bogdanos, Gina Whitney, Sandy Underwood and Joe Farmer.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.