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ABSTRACT

A procedure is described for the uniform removal of very thin sections of metal surfaces by means of electrolysis. Equipment requirements and the various parameters affecting operation are first considered, and the results of applying the technique to studies of solid state diffusion are then discussed. The technique appears to offer considerable promise for evaluating chemical changes at metal surfaces which have taken place as a result of corrosion or diffusion processes.

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AN EVALUATION OF ELECTRO-MACHINING FOR THE ANALYSIS OF METAL SURFACES

INTRODUCTION

The determination of the chemical composition of metal surfaces is an important adjunct to experimental investigations dealing with both corrosion and diffusion processes. In each type of investigation it is often necessary to obtain a complete compositional analysis of regions near affected surfaces within depths that amount to only a few mils. While the removal of these affected areas for analysis can be accomplished by conventional machining methods, the small magnitude of affected areas seriously complicates the use of such methods. The specimen geometries which are convenient for test purposes often are impossible to machine to close tolerances, and the introduction of foreign particles from the tool bit or lubricant during machining imposes a serious source of error in samples obtained by this method. Also the minimum depth of cut attainable with this method often exceeds that which is needed for a proper evaluation of surface areas. Finally machining to rigid tolerances is difficult where a high surface hardness is encountered, as is the case with carburized materials or certain refractory metals.

The use of electrolysis for the controlled removal of metal surfaces showed promise of avoiding all of the above problems. However, an electro-machining technique, to be satisfactory, must satisfy at least the following requirements. First, the rate of surface removal must be uniform; that is, the rate of transfer of components of the metal into the electrolyte must be constant at every point on the metal surface. Further the electrolysis should not be selective in the removal of metal constituents, but rather the ratios of elements entering the electrolyte should agree stoichiometrically with ratios existing in the metal. Finally the rate of metal removal must be controllable and reproducible, so that selected depths of machining can be confidently established in terms of current passage and machining time. The degree to which electro-machining fulfills each of these requirements is the subject of this evaluation.

PARAMETERS AFFECTING ELECTROMACHINING

Electromachining, or the removal of metal surfaces through electrolysis, is effected by the ionization of surface atoms and their passage through a suitable electrolyte as cations. The technique under proper conditions of voltage, current, and temperature can be used to smooth or polish a metal surface, and toward this

end it has been applied industrially for many years. The developments worked out in conjunction with this application, i.e., electropolishing, provided an excellent background from which to begin electro-machining experiments. It should be pointed out, however, that for certain electromachining operations, namely those involving extremely thin surface cuts, it is important that polishing of the metal surface does not take place. It was therefore necessary to investigate also those conditions for which smoothing of the metal surface was eliminated.

The optimization of conditions for electromachining begins naturally with a consideration of the processes which take place at the metal surface during electrolysis. A typical electrolytic cell which may be used to degrade a metal surface is sketched in Fig. 1. Also shown are the oxidation-reduction reactions which take place in the cell. As an increasing voltage is applied across the anode and cathode of the cell, the current density will follow generally the relationship shown in Fig. 2. As voltage is impressed on the cell and dissolution of metal occurs, a boundary layer (usually an oxide or hydroxide) forms adjacent to

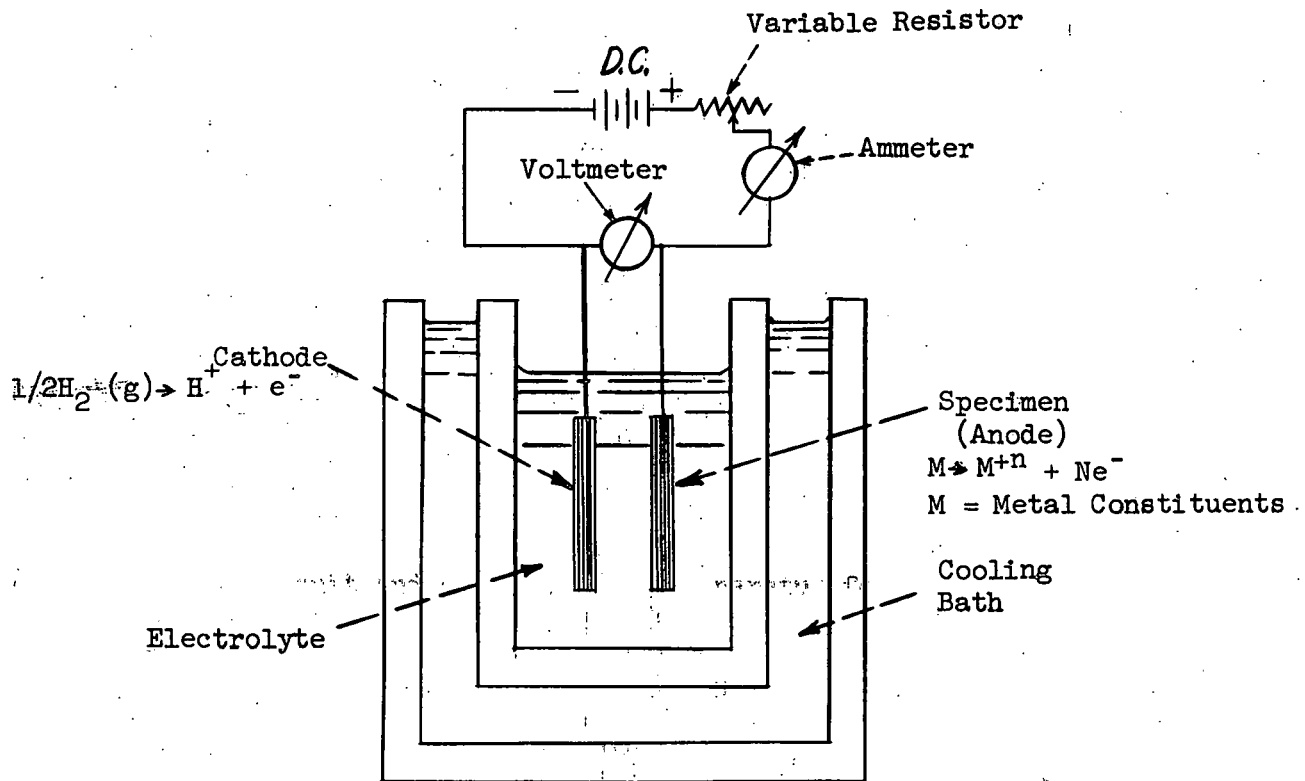


Fig. 1 Electrical Circuit and Arrangement of Apparatus for Electrolytic Machining.

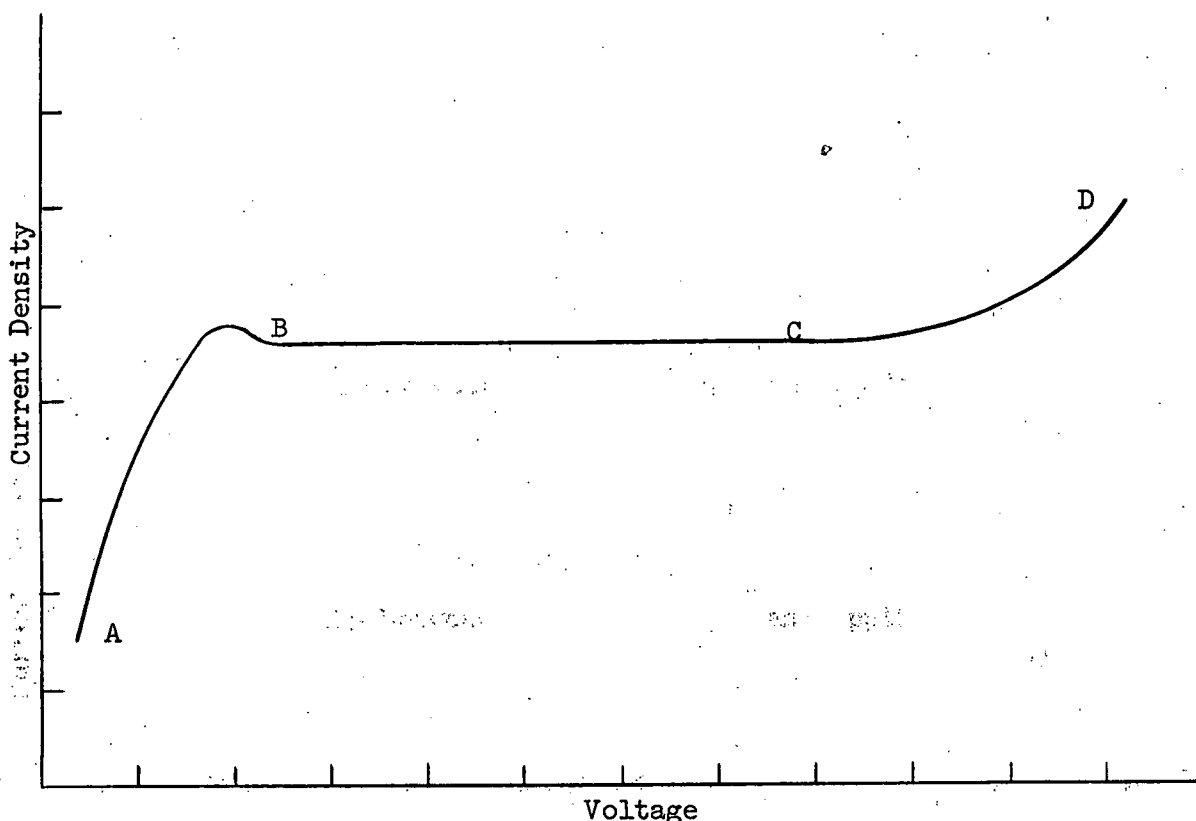


Fig. 2 Relationship Between Current Density and Applied Voltage For an Aqueous Electrolytic Cell Such as Shown in Fig. 1

the metal (anode) surface. This boundary layer, which is of higher electrical resistance than the bulk of the electrolyte, increases in thickness with increasing voltage, so that the increase in current with voltage is not constant, but is of a decreasing order. A voltage (and corresponding film thickness) is eventually achieved where changes in the rate of boundary film formation and the rate of diffusion of cations into the bulk electrolyte offset one another. Within this range current remains relatively constant with further increases in voltage.

As the boundary layer or film gains in thickness, it tends to assume a level profile relative to the anode surface; that is, the film becomes thicker in depressed areas of the anode surface than in elevated areas. Thus the electrical resistance is lower on the elevated areas than on the depressed. Under a given potential the current density at the peaks and ridges of the surface will be

greater than at the valleys, and a gradual smoothing of the anode surface occurs.

It will be noted in Fig. 2 that region B-C, in which changes in voltage produce no effective change in current density, is followed by a region C-D, where changes in voltage again have an appreciable effect on current. In the latter region, voltage is sufficiently high to induce hydrolysis of the solution (reaction 4 in Fig. 1). In view of this competing means for the conduction of current, it obviously becomes quite difficult in range C-D to establish a firm relationship between current density and the rate of metal transfer between anode and solution. Thus this range is to be avoided if reproducible machining tolerances are a prerequisite.

From the above considerations it is evident that cell voltage is an extremely important parameter in controlling the electro-machining process. The above discussion further infers an advantage in a relatively low cell voltage for avoiding polishing effects and solution electrolysis. The temperature of the electrolyte is another important variable in the electro-machining process, since temperature strongly influences the stability of the anodic film or boundary layer. An increase in temperature decreases the thickness of the film relative to a given current density and also increases the rate of dissolution of the anodic film.

The selection of a proper electrolyte no doubt constitutes the most formidable problem in the course of developing an electromachining process for a given metal. The two most important requirements of the electrolyte are that it not undergo electrolytic decomposition (other than reduction of hydrogen ions) at voltages necessary for machining and that it be chemically inert with respect to the metal specimen. Many excellent electrolytes have been developed in conjunction with electropolishing processes, and these provide a good basis from which to select electrolytes for machining purposes.

EQUIPMENT REQUIREMENTS

If used to obtain a uniform rate of surface removal, an electrolytic cell must be designed so that the potential drop and attendant current density between the anode and cathode are the same at any point on the anode. This requirement is directly satisfied by maintaining a similar contour between anode and cathode, so that a uniform distance exists between the two electrodes. A second approach is to rotate the anode relatively to the cathode, so that after a given period of time all points of the anode

surface have been subjected to the same effective voltage drop. This technique is discussed further in a subsequent section.

The cathode may be fabricated of any material which is chemically inert in the electrolyte and which possesses a reasonable electrical conductivity. Platinum or graphite make ideal materials for most uses. The cell current and voltage usually can be supplied by a D. C. source with variable voltage up to about 10 volts. Current requirements for the majority of experiments for which the electromachining techniques are suited are generally low, and in most cases currents of less than one ampere are required.

Temperature control of the electrolyte bath, as discussed in a preceding section, is quite important and can normally be accomplished in one of two ways. A portion of the electrolyte can be continuously circulated through glass tubing immersed in a constant temperature water bath, or a coil containing fluid maintained at a pre-set temperature can be set in the electrolytic cell to either heat or cool the electrolyte. It should be recognized that, if current densities are relatively high, appreciable heating of the electrolyte can occur due to energy losses associated with current flow through the electrolyte.

In designing an apparatus for electro-machining, consideration must also be given to the volume of the electrolyte. A composition change naturally results from the build up of metal ions in the electrolyte and can appreciably change the characteristics of the cell. Avoidance of this problem can be realized through a relatively large volume of electrolyte or by replacement of the electrolyte at intervals during machining.

RESULTS OF ELECTROMACHINING EXPERIMENTS

Initial interest in electromachining developed from studies of the high temperature diffusion rates of chromium in nickel-base alloys, which have been carried out both by the Battelle Memorial Institute and the Oak Ridge National Laboratory in support of the molten salt reactor program. These studies utilize a radio-isotope, chromium-51, to track the movement of chromium atoms as a function of both time and temperature over the range 600°C-900°C. A pre-determined percentage of radio active atoms is maintained at the surface of the material in the course of these experiments, and the resultant pick-up of radio activity by the alloy is then monitored. Although

an indication of diffusion rate can be derived by merely counting the radio-activity of the specimen after test, self-shielding effects make it desirable to remove layers of the surface where diffusion has occurred and to count the electrolyte which contains the constituents of these various layers. The tests are conducted within a closed loop so that diffusion takes place at the inside walls of 5/8" I.D. section of tubing. It was therefore necessary to develop an apparatus for machining the inside surfaces of commercial tolerance tubing. A schematic drawing of the electro-machining apparatus used for these experiments is shown in Fig. 3. Note that a graphite rod, used as a cathode, is located within the metal specimen and that the specimen is rotated around this rod. By this technique problems which might arise because of misalignment between the graphite and the central axis of the specimen are alleviated, since, in revolving around the rod, every point on the metal surface tends to see effectively the same average distance between it and the graphite cathode.

The electrolyte used in these studies was composed of 65 parts of H_3PO_4 , 15 parts of H_2SO_4 , and 20 parts of distilled water. It was determined by plotting current density-voltage relationships at several bath temperatures and metallographically examining test specimens that the most reproducible and uniform surface removal was accomplished at a current density of 100 milli-amps/in.² and 90° F. Measurements of both the weight and wall thickness losses of the specimens indicated that machining under these conditions was done at a rate of 1/2 mil/hr. As can be seen in Fig. 4, in which the measured weight losses of Inconel capsules are plotted as a function of test time, the rate of metal removal tended to be very uniform with time. Changes in wall thickness were also found to be uniform from the top to bottom of the capsule as well as around the circumference. The metallographic appearance of an Inconel specimen after the removal of a 1 mil surface layer by electromachining is shown in Fig. 5. It will be noted that the surface is free from pitting, and the surface contour shows very even removal at least over the area included in the photomicrograph.

The results which have been obtained in applications of the electromachining technique to the diffusion studies previously cited have likewise been encouraging. Profiles of the surface concentration of radio-chromium which have been determined from countings of the electrolyte after successive machinings agreed very well with profiles which were calculated from the total count of radio-activity in the

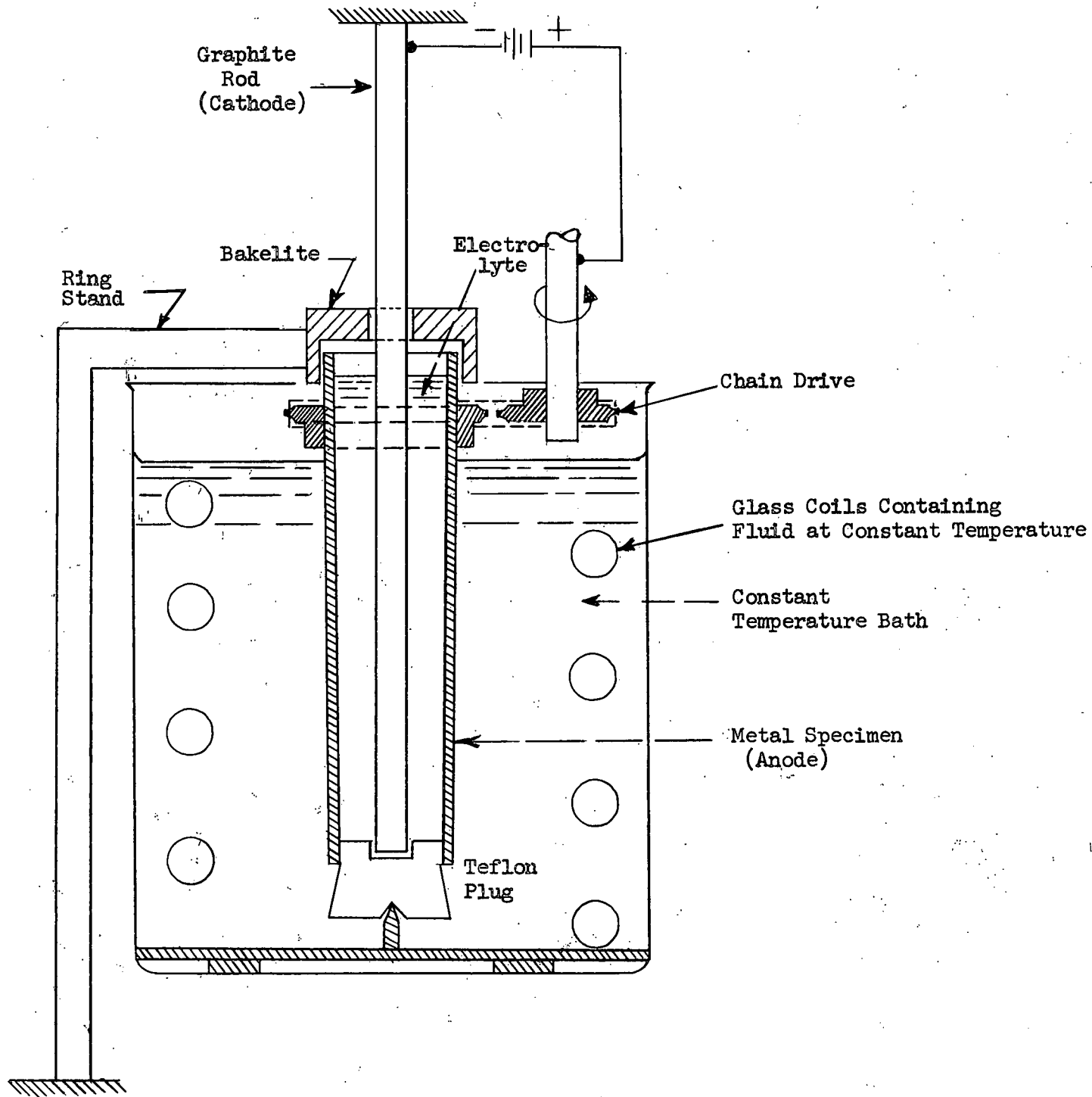


Fig. 3 Schematic Drawing of Apparatus Used to Machining Inside Surfaces of 3/8" Sch. 10 Pipe.

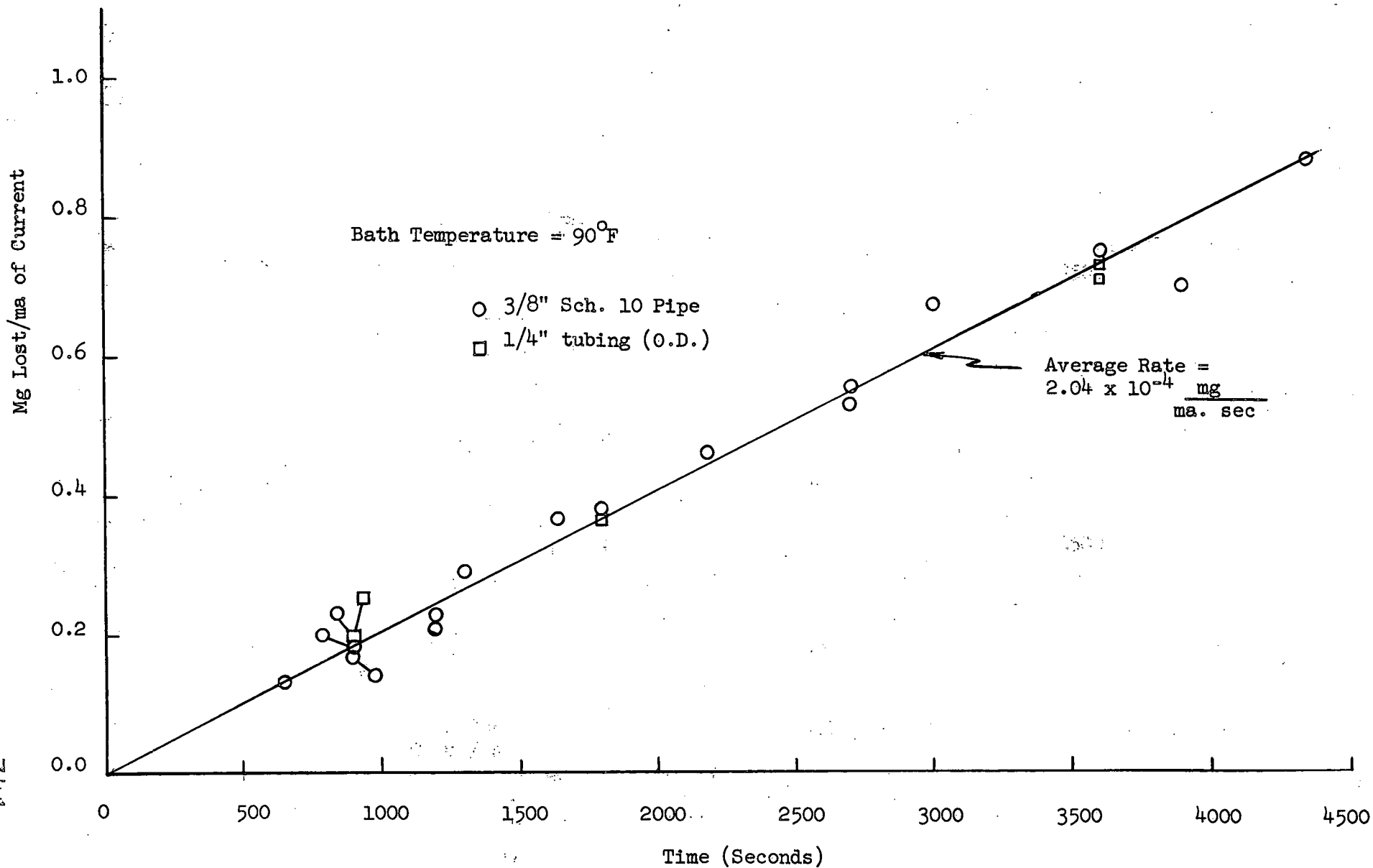


Fig. 4 Weight Losses Occurring for Inconel Specimens as a Function of Machining Time. Current Density was Maintained at 100 ma/in².

60 THZ

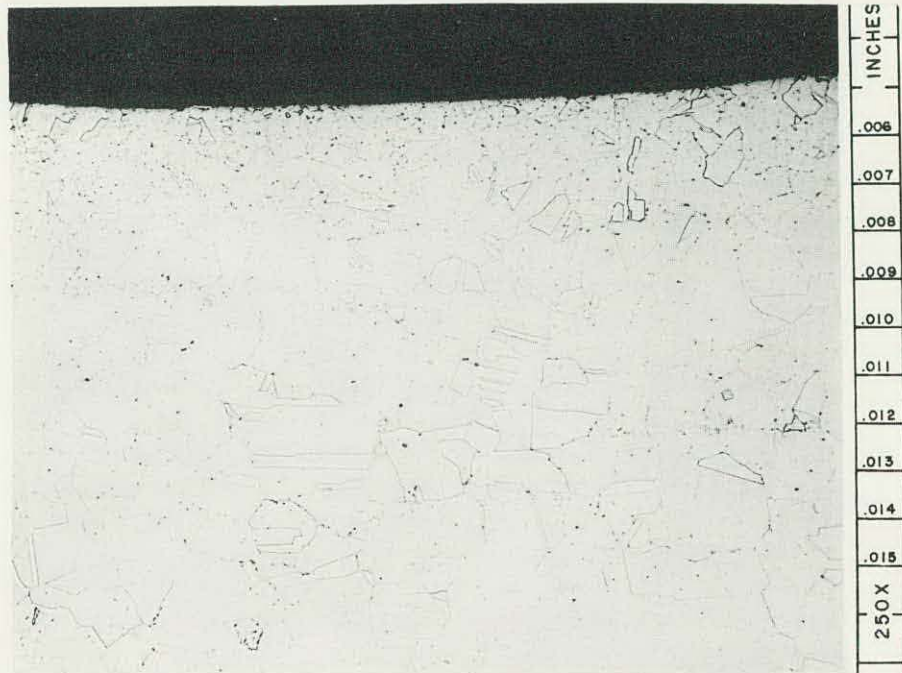


Fig. 5 (T-16642) Inconel Tubing Electropolished at 100 ma/in^2 for 60 min. at 90°F . Total penetration was $\sim 1 \text{ mil}$. Mag. 250X; Etchant: Modified Aqua Regia.

specimens. It is of interest that the depths of machinings involved in these studies have been on the order of only a few microns.

CONCLUSIONS

Electromachining appears to be a very practical means of studying the surface chemistry of metals and alloys which have been affected by the processes of corrosion or diffusion. Parameters have been established for the successful application of electromachining to nickel base alloys containing chromium in solid solution, and it is felt that the techniques can easily be extended to other metal systems, particularly those involving alloys of the solid solution type. It is also planned to investigate the potential of this technique for determining surface concentrations in alloys composed of two or more phases; in particular it is hoped that this method can be applied to studies of the carburization rates of various high temperature alloy systems.

REFERENCES

Listed below are references which were used in the preparation of this report and which should be helpful in an extension of the electro-machining technique to new materials.

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