

# Electropolishing of Copper Alloys in Phosphoric Acid Solutions with Alcohols

by E. Pircher\*, M. Ruíz Martínez, S. Hansal & W. Hansal

The electrochemical polishing process of ternary copper alloys (15% Mn, 15% Zn) in phosphoric acid-based electrolytes has been studied. The effects of phosphoric acid concentration and the presence of different alcohols (methanol, ethanol, propanol and butanol) in the polishing electrolyte, on the polarization diagrams and the metal removal rate were studied. Additionally, Hull cell tests were carried out in order to investigate the relationship between the appearance of the polished surfaces and the current density. The polished surfaces were characterized by environmental scanning electron microscopy and atomic force microscopy.

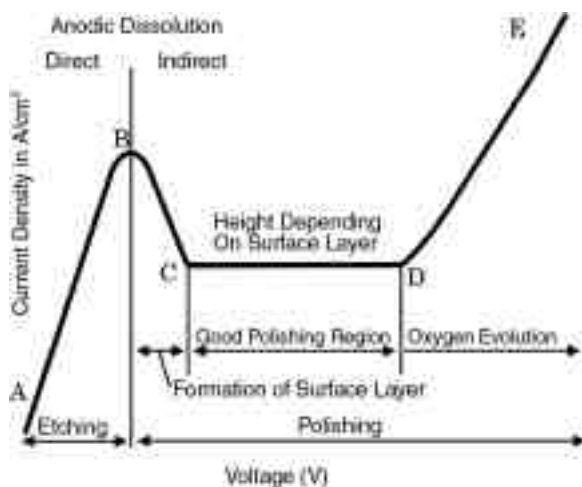


Fig. 1—Schematic of a current-voltage-curve in the anodic region:

- A-B: etching of grain boundaries.
- B-C: formation of a passivating oxide layer and a concentrated diffusion film at the surface.
- C-D: region suitable for the electrochemical polishing process.
- D-E: transpassive region with strong oxygen evolution. Also useful for electropolishing.

Smooth, shiny metal surfaces are often required for industrial or decorative use. Electropolishing provides an effective method, that not only results in bright, smooth surfaces,<sup>1</sup> but also guarantees high purity of the resulting surface (no traces of polishing material like aluminium oxide or diamond). Electropolishing is generally defined as the improvement of the surface finish of a metal caused by anodically polarizing it in an appropriate solution.<sup>2</sup> The metal to be polished is immersed in a polishing solution that must be carefully chosen for each system, anodically polarized and dissolved by applying a specific amount of current for a fixed period of time. This dissolution must be performed in such a way that irregularities such as holes, hills or scratches are removed and the surface becomes smooth and bright.

In order to produce a truly flat surface, both the macroscopic and microscopic irregularities must be removed. Therefore, the functions of an ideal polishing process can be distinguished as:

1. Smoothing the surface by eliminating large scale irregularities (above one micron in size) and
2. Brightening the surface by removing smaller irregularities (of size smaller than one micron down to several hundredths of a micron).

A successful polishing process must combine both of these functions in an effective and appropriate way.<sup>3</sup>

A characteristic polarization diagram can be determined for each polishing process, generally referred to as a “current density/voltage” diagram, by simply varying the potential and measuring the resulting current flowing through the system.

A schematic “current density/voltage” diagram is shown in Fig. 1.<sup>4</sup> Different potential regions can be distinguished, resulting in completely different surface properties. Between A and B etching occurs preferentially, and grain boundaries are attacked. Beyond B the surface becomes passive. A diffusion layer is formed at the metal surface, which is necessary for the polishing process. The potential between C and D represents the best polishing region,<sup>5</sup> especially when metal alloys, containing both noble and non-noble metals, have to be polished. The limiting current depends on the nature of the diffusion layer and is there-

## Nuts & Bolts: What This Paper Means to You

Electrochemical processes are just as important in removing metal surfaces as they are in depositing on them. The newly-formed AESF Emerging Technology Subcommittee on Electrochemical Metal Removal attests to this. This article deals with work on electropolishing, specifically on ternary copper alloys. The use of various alcohols added to phosphoric acid-based baths is studied here. It shows us that the concerns with metal removal are reminiscent of concerns with metal plating... the final surface is the product.

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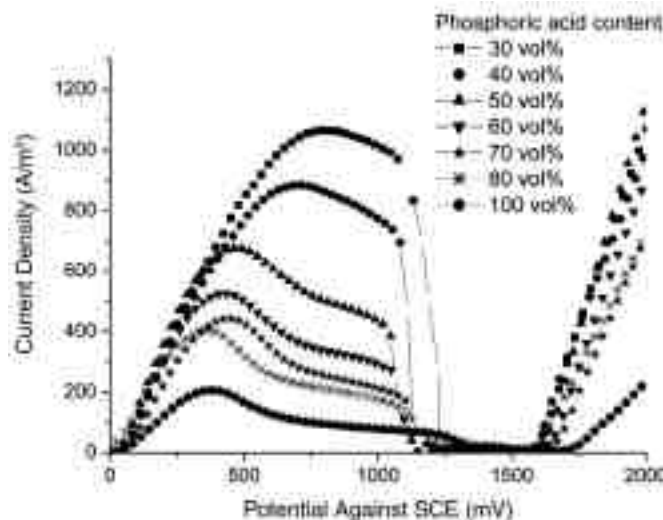


Fig. 2—Current-voltage diagrams of electrolytes with different phosphoric acid concentrations.

for a function of electrolyte composition, surface morphology of the substrate, temperature and flow conditions. In the transpassive region (beyond D) it is also possible to perform electrochemical polishing (especially when polishing highly alloyed steel surfaces), but there the appearance of “zebra stripes” and other surface patterns because of enhanced gas evolution (oxygen) is very likely to occur. In some cases the evolving oxygen can help remove smut adherent to the surface.

Improved polishing electrolytes for industrial use contain additional components such as polyethylene glycol or glycerol<sup>6</sup> to modify the viscosity, alcohols, acids, surfactants and complexing agents to alter the surface interactions and solubility of the reaction products. All of these additional components influence the current-voltage characteristics in different ways, *e.g.* by extending and shifting the polishing plateau, raising or lowering the limiting current, and so forth.

Common electrolytes for polishing pure copper surfaces are based on phosphoric acid and contain at least 200 g/L of this chemical.<sup>7</sup> In addition, chromic acid, sulphuric acid, sodium triphosphate and potassium cyanide have been used individually or together with H<sub>3</sub>PO<sub>4</sub>. A high phosphoric acid concentration and a slow electropolishing rate are some disadvantages of the phosphoric acid solution.<sup>8</sup> The aim of this work was to systematically investigate the influence of different alcohols (methyl, ethyl, isopropyl and butyl alcohol) on the polishing properties of phosphoric acid-based electrolytes for polishing copper alloys.

## Experimental

For all experiments, special copper alloy sheets containing manganese (>10 %) and tin (>10 %), were used as substrates. All electrolytes were based on phosphoric acid and are listed in Table 1. Each

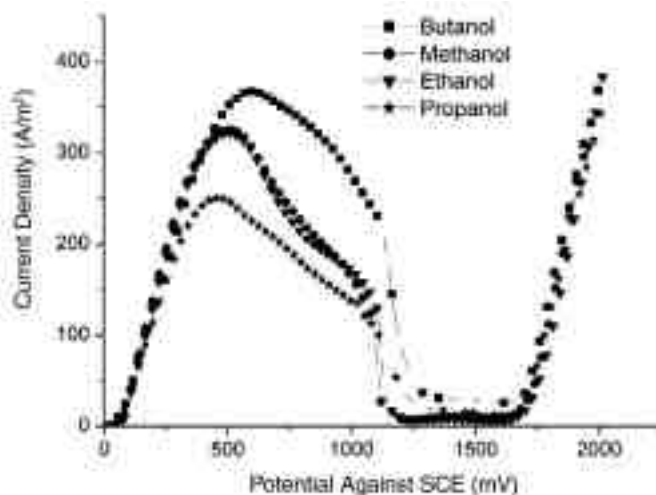


Fig. 3—Current-voltage diagrams of phosphoric acid-based electrolytes containing alcohols.

alcohol under study was added to a phosphoric acid solution of 50 vol% of 85 wt% phosphoric acid stock solution in order to obtain alcohol contents of 30 and 50 vol%. Distilled water was used in preparing these solutions.

Additionally, in order to compare these electrolytes with straight phosphoric acid solutions, electrolytes with different phosphoric acid concentrations (30, 40, 50, 60, 70, 80 and 100 vol%) were prepared. For our tests, the copper alloy plates were immersed in 250 mL of the electrolyte under study. The polishing processes were performed at room temperature with a polished copper sheet as a cathodic counter electrode with an interelectrode spacing of 3 cm (1.2 in.), aligned parallel to the anodic copper alloy sheet. A fresh solution was made for every experiment. For measuring the current-voltage-characteristics and metal removal rates a computer-controlled galvanostat/potentiostat was used. For the Hull cell tests, a common 250 mL Hull cell system was used. The conductivity of the electrolytes was measured using a standard conductivity cell.

## Results & Discussion

### Potential-current Characteristics

The potential-current characteristics of each electrolyte were recorded using a potential range of 2000 mV versus a standard calomel electrode (SCE) at a scanning speed of 5.0 mV/sec. In contrast to pure copper, the polishing region of the ternary copper alloy was interrupted by a zone of total passivation between ca. 1200 and 1600 mV.

For electrolytes with different concentrations of phosphoric acid (Fig. 2), the position of the peak maxima depends on the acid concentration. Within the range between 30 and 100 vol% phosphoric acid concentration, a higher acid content shifts the position to less

Table 1  
Composition of the Electrolytes Used

Electrolyte	A	B	C	D	E	F	G	H
Phosphoric acid (85 wt%)	50 vol%	50 vol%	50 vol%	50 vol%	50 vol%	50 vol%	50 vol%	50 vol%
Methanol (99.8 vol%)	50 vol%				30 vol%			
Ethanol (99.8 vol%)		50 vol%				30 vol%		
2-Propanol (99.5 vol%)			50 vol%				30 vol%	
Butanol (99.0 vol%)				50 vol%				30 vol%
Water					20 vol%	20 vol%	20 vol%	20 vol%

**Table 2**  
**Conductivity of Aqueous Solutions of Phosphoric Acid**

Phosphoric acid (vol%)	mS/cm	Phosphoric acid (50 vol%) Water (20 vol%) Alcohol (30 vol%) Plus Balance of:	mS/cm
30	199	Methanol	91
40	222	Ethanol	76
50	215	Propanol	72
60	195	Butanol	76
70	165		
80	137		
100	93		

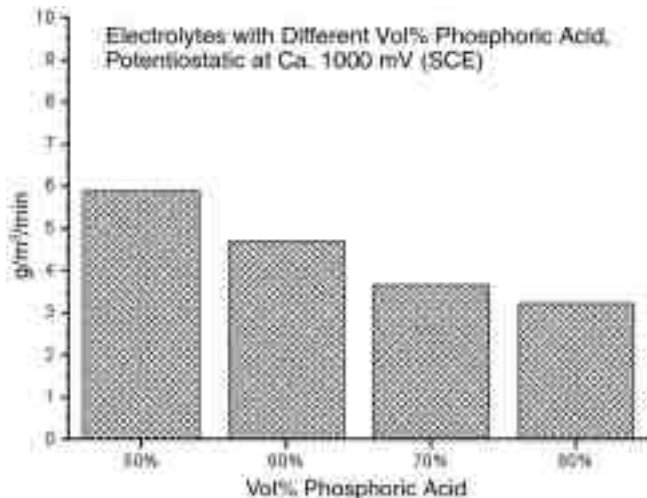


Fig. 4—Influence of the phosphoric acid concentration on the removal rate under potentiostatic conditions (at 1000 mV<sub>SCE</sub>).

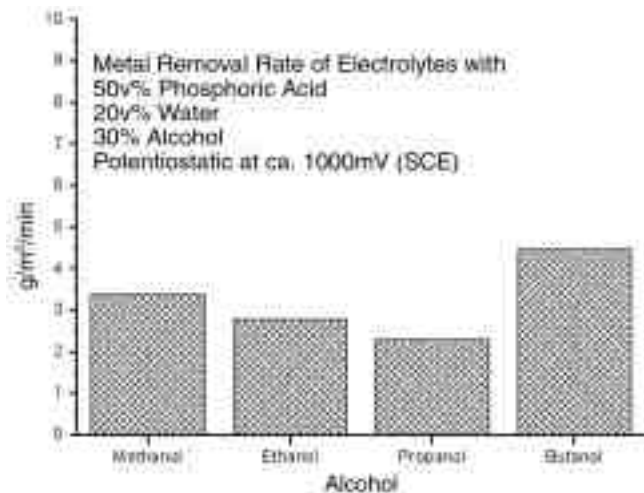


Fig. 5—Influence of alcohol on the metal removal rate (potentiostatic conditions at 1000 mV<sub>SCE</sub>).

anodic potentials while the polishing plateau is more pronounced. In theory this should favor a good and uniform electropolishing process, which was confirmed by the Hull cell tests (to be discussed later). For the 30 and 40 vol% phosphoric acid polishing electrolytes, there was no clear plateau observed. In the range between 50 to 80 vol% phosphoric acid, the polishing plateau became more defined, leading to a flat and broad polishing region for a phosphoric acid content of 100 vol%. Parallel to this relationship, the total current density of the polishing reaction significantly decreases with increasing phosphoric acid content. This is in good accordance with the decrease of conductivity at higher concentrations of phosphoric acid (Fig. 3).

The potential-current characteristics were similar for the alcohol-containing electrolytes (Table 1, solutions E-H). The only exception was the electrolyte containing butyl alcohol. In that case, the maximum of the curve shifted toward a more anodic voltage and the gap, where total passivation occurred, was significantly smaller (compare also with the corresponding Hull cell picture in Fig. 8).

The limiting current density seemed to have no correlation with the chain length of the alcohol and decreased in the order butyl > methyl ~ ethyl > propyl alcohol.

Compared to the electrolyte containing only phosphoric acid in aqueous solution, the electrolytes containing alcohol had smaller resultant current density values, as shown in Figs. 2 and 3. The maximum current density of 6.5 A/dm<sup>2</sup> (60.4 A/ft<sup>2</sup>) was found for the phosphoric acid-based electrolyte with an acid concentration of 50 vol% while a similar electrolyte containing 30 vol% alcohol led to current densities between 2.5 and 3.6 A/dm<sup>2</sup> (23.2 and 33.4 A/ft<sup>2</sup>).

### Metal Removal Rate

The metal removal rate was measured by weighing a sample with a defined surface area, using a microbalance, polishing both sides at a potential of about 1000 mV<sub>SCE</sub> for 10 min and weighing the sample again. The average weight loss after polishing of four replicate samples was taken as the metal removal rate, given in g/m<sup>2</sup>/min.

Measurements using electrolytes of different phosphoric acid concentration showed that the removal rate decreased nearly linearly with the phosphoric acid content, which is in good agreement with the results of previous voltage scanning experiments where the removal rate was proportional to the limiting current, correlating well with the potentiostatic experiments (see Fig. 4).

For the 30 vol% alcohol-containing electrolytes (see Table 1, electrolytes E-H) a good agreement between individual experiments was noted (see Fig. 5). The butanol-containing electrolyte exhibited the highest current density (See the potential-current characteristic.) during the polishing process and also the highest metal removal rate of the four alcohol-containing electrolytes tested, although the conductivity of this electrolyte was rather low. A possible explanation for this behavior could be the function of butanol as good complexing/solvating agent for the dissolved copper ions. The difference between the metal removal rates of methanol-, ethanol- and propanol-containing electrolytes was very small and may have been related to the difference in the conductivity of the solutions (see Table 2).

### Hull Cell Tests

Hull cell experiments were performed in order to get a quick overview of the polishing process and its dependency on the current density. Polishing using aqueous phosphoric acid electrolytes with acid concentrations below 50 vol% proved that the polishing effect took place only in high current density regions. Using these bath compositions, the polishing region was preceded by a large region where etching of the surface occurred. A much better polishing performance was attained at phosphoric acid concentrations between approximately 60 and 80 vol%. Above 80 vol% phosphoric acid, the polishing effect was very slow because of the low limiting current, so it was impossible to get good results within a reasonable time. The legend for the Hull cell patterns is shown in Fig. 6. Figure 7 shows the Hull cell patterns obtained after polishing the copper alloys in phosphoric acid-based electrolytes at different acid concentrations.

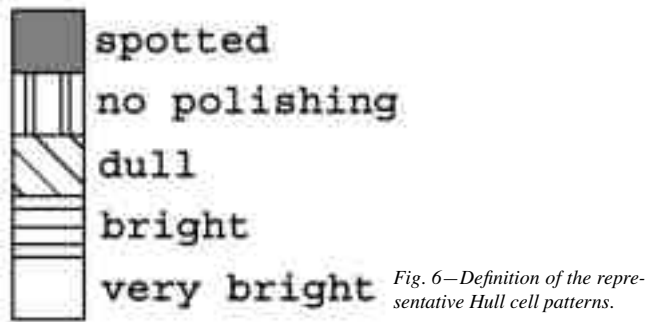


Fig. 6—Definition of the representative Hull cell patterns.

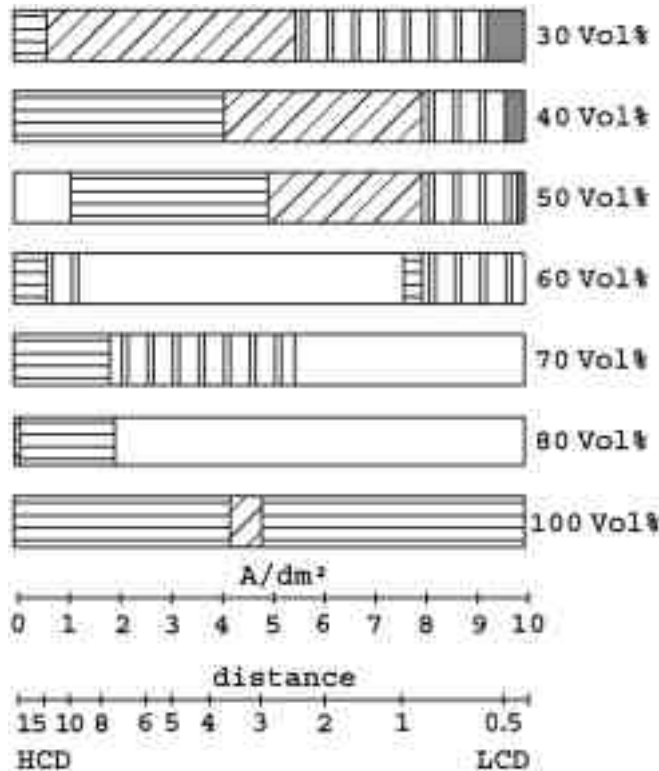


Fig. 7—Hull cell pictures of phosphoric acid electrolytes of different concentrations.

When different alcohols were added to the electropolishing bath, the regions of good surface polishing were shifted to lower current densities, while the general polishing performance was increased. Adding 50 vol% of different alcohols to a 50 vol% aqueous phosphoric acid solution (electrolytes A-D in Table 1) gave good polishing effects at current densities below 0.5 A/dm<sup>2</sup> (4.6 A/ft<sup>2</sup>). The bright surface polishing region was approximately the same for methanol, ethanol and propanol. The addition of butanol led to an extraordinarily extended polishing zone, up to current densities of approximately 3.0 A/dm<sup>2</sup> (27.9 A/ft<sup>2</sup>). Propanol-containing electrolytes also allowed electropolishing in the transpassive region at high current densities. The regions of polishing and passivation were shifted to lower current densities with longer alkyl chains of the alcohols, with the exception of butanol.

Adding 30 vol% of the alcohols studied to a 50 vol% aqueous phosphoric acid solution (electrolytes E-H in Table 1) led to similar results (see Fig. 8). The electropolishing region was shifted to higher current densities of 2.0 A/dm<sup>2</sup> (18.6 A/ft<sup>2</sup>) for all four alcohols studied. The butanol-containing electrolyte showed a slightly different behavior again, providing a polishing region between 1.0 and 4.0 A/dm<sup>2</sup> (9.3 and 37.2 A/ft<sup>2</sup>). Propanol-containing electro-

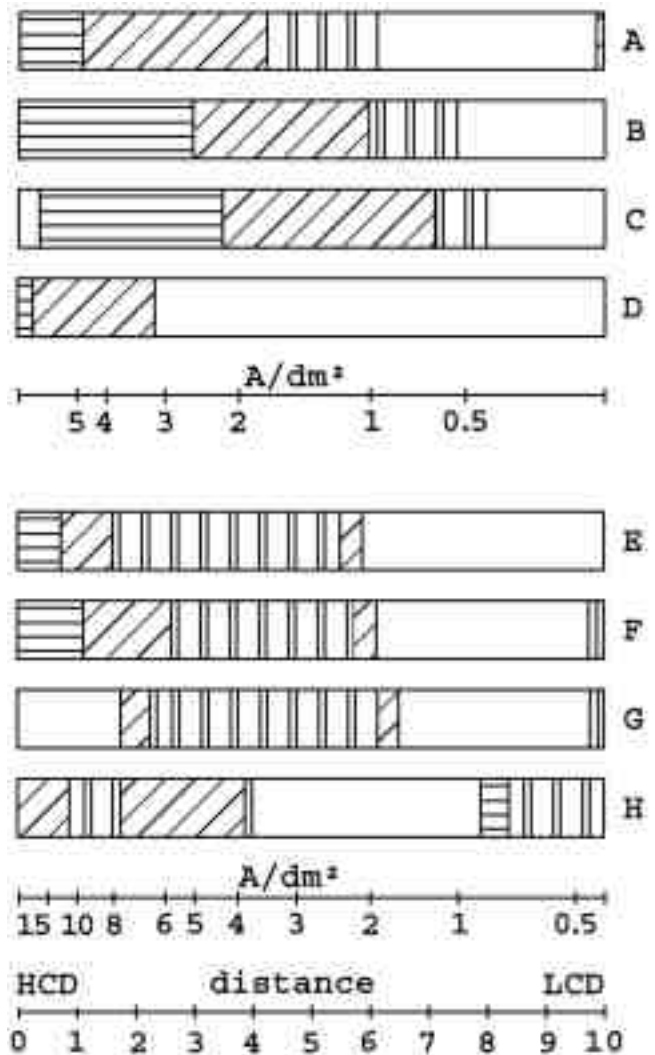


Fig. 8—Hull cell patterns of polished surfaces using different electrolytes. (Electrolyte compositions are listed in Table 1.)

lytes again exhibited an electropolishing region in the transpassive region (at high current densities).

### Sample Characterization

In addition to the electrochemical and optical characterization of the electropolished surfaces, the samples were characterized by environmental scanning electron microscopy (ESEM) and atomic force microscopy (AFM, using a non-contact mode) in order to determine the surface topography and the average surface roughness before and after electropolishing.

Figure 9 shows ESEM-pictures of an electropolished copper alloy surface after 5.0 min of polishing in a 70 vol% phosphoric acid electrolyte compared with an unpolished surface. There is a remarkable difference in the surface morphology. After electropolishing nearly all of the irregularities were removed, resulting in a smooth, homogenous surface. Only the major defects were not completely removed after this rather short polishing time. The AFM measurements revealed the same result. Figure 10 shows representative AFM pictures of copper alloy surfaces before and after electropolishing. The surface roughness was dramatically diminished by the electrochemical polishing process. The value of the average surface roughness decreased from  $R_A = \sim 140$  nm to a value of  $R_A = \sim 11$  nm.

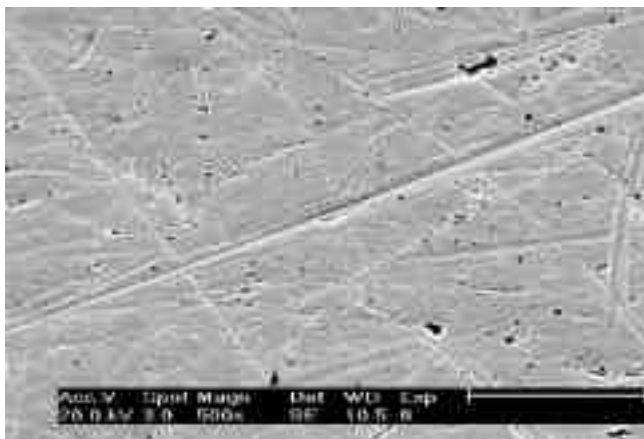


Fig. 9—ESEM pictures (magnification 500x) of a copper alloy surface (a) before and (b) after electropolishing.

## Summary

Hull cell experiments reveal that in aqueous phosphoric acid electrolytes, good polishing results are only obtainable with a minimum acid content of 60 vol%, which is in good accordance with the polarization curves. An examination of the polarization curves shows that these results are understandable. The characteristic polishing plateau became significant at acid concentrations above 50 vol% and was shifted towards favorable lower anodic potentials with an increase of the acid content. The best polishing results were obtained for concentrations between 70 and 80 vol%.

Addition of alcohols to electrolytes with an acid content of 50 vol% improved the polishing qualities of such “low acid level”-polishing solutions. The current densities in the polishing zone (2.0 to 4.0 A/dm<sup>2</sup>; 18.6 to 37.2 A/ft<sup>2</sup>) and the beginning of the potential range for polishing (about 500 mV<sub>SCE</sub>) were in the same region as the aqueous phosphoric acid electrolytes with an acid content between 60 and 90 vol%.

The only exception to this trend was the butanol-containing electrolyte, which showed a reduced characteristic polishing plateau similar to the electrolyte with low acid content. Still, we found acceptable polishing results in the Hull cell tests which produced smooth and shiny surfaces at a higher metal removal rate.

Additional studies with additions of 50 vol% alcohol in the Hull cell, gave a rather poor polishing performance, proving that a certain amount of water was necessary for a polishing electrolyte to obtain acceptable polishing results.<sup>9</sup>

Despite the lower conductivity of alcohol-containing electrolytes, resulting in lower values of the limiting current and therefore longer polishing times, the addition of alcohols improved the polishing performance. Shinier and smoother surfaces can be produced even at lower acid concentrations in the electrolyte.

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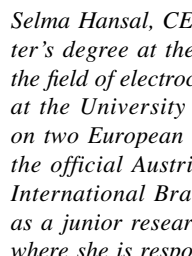
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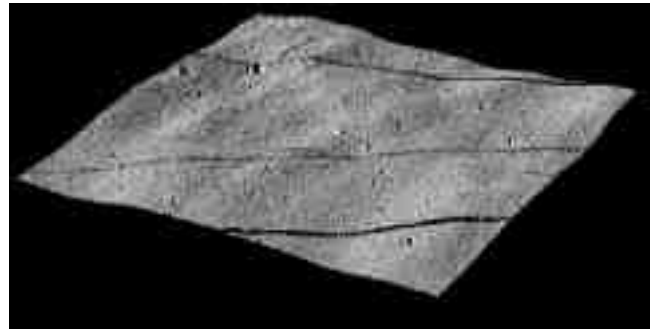
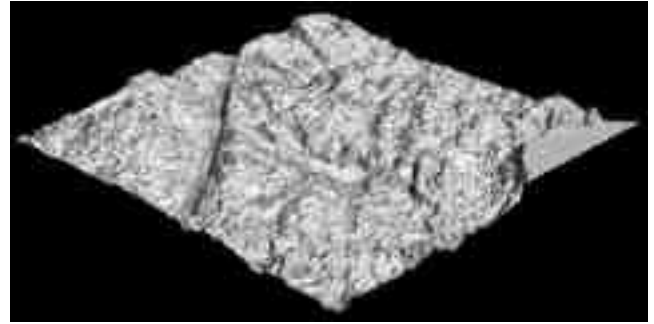


Fig. 10—AFM images of copper alloy surfaces (a) before and (b) after electropolishing.

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