# Optimization of the Preplating Processes in the Fabrication of Electrolessly Tin-Coated Copper Tube

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**Despite the recent extensive examination of electroless coatings, the effect of the preplating processes on the formation of electroless coatings has remained unresolved. The ability of different preplating processes, degreasing and pickling, to clean the contaminated copper surface before deposition was studied by contact angle determinations, residual oil measurements, and potentiostatic polarization cycles. The influence of preplating processes on the buildup of electroless tin coatings and subsequent deposit structure was studied by scanning electron microscopy. Alkaline degreasers were found to effectively eliminate the organic soil from the surface, thus facilitating uniform coating nucleation and good adhesion properties. Pickling gave rise to a regular coating appearance throughout the structure. In addition, the applicability of contact angle measurements for studying the efficiency of cleaning treatments was demonstrated.**

**Keywords** preplating processes, electroless tin coatings, copper tube, surface, cleaning, pickling

## 1. Introduction

Electroless tin coatings provide copper water tube with cathodic corrosion protection and serve as a barrier between the base metal and an aggressive environment. The corrosion protection capability of coating heavily relies on a uniform coating structure. Yet, despite this importance, many factors influencing the coating structure formation still remain obscure. One unknown area consists of preplating processes, which involve the removal of surface contamination by various treatments. This paper addresses the role of preplating processes in coating structure formation and describes some tools for achieving an optimal preplating procedure.

Electroless coatings find a wide range of applications in corrosion and wear protection technology as well as in the electronics industry. Their usefulness derives from their good surface properties, ability to produce uniform coatings with high throwing power, and suitability for complex substrate surface shapes.[1] The increasing severity of corrosion and wear environments combined with the ever-developing field of microelectronics has widened the market for electroless coatings. On the other hand, as the number of metals available as electroless coatings has increased, new approaches have been sought for them.

Recent concerns over copper dissolved in drinking water have posed the question of controlling the internal corrosion of copper water tubes by coating the inner tube surface with electroless tin deposit. Restricted copper release combined with other environmental pressures and the quality criteria set on products by consumers enhance the importance of a reliable coating performance and, thus, uniform coating structure.[2] The structure is influenced by three preliminary attributes, which all act independently to form an integrated system: preplating procedures, the actual coating process, and postplating treatments.[3] Although the deposition process itself has been widely studied, and a number of papers deal with the postplating treatments of nickel deposits, only minimal attention has been paid to the relation between the preplating procedures and the coating structure. This paper discusses the preplating processes and aims at optimizing the coating structure and performance by optimizing the preplating processes.

In preplating process optimization, the complete production route of the uncoated component has to be taken into consideration in order to understand the sources of surface contamination. In general, the functional metal surface usually consists of several contaminant layers on the base metal itself. These contaminant layers have a detrimental influence on the production or the properties of tin coating.[4,5]

An outermost contamination layer consists of oil, soil, and greases from prior processing.[5,6] In hard-drawn copper tubes, this layer comprises drawing oils from the tube production sequence. Trichloroethylene has traditionally been used to clean the copper surface of drawing lubricants,[5] but due to its inefficiency in preparing the copper surface for electroless plating and the environmental aspects,[6,7] alternatives are being sought. Other cleaning procedures suggested to be capable of removing drawing oils from the copper surface include emulsion cleaning, acid cleaning, and alkaline degreasing.[4] An inner contaminant film is the thin reaction layer of oxides, sulfides, and hydroxyls formed as a result of chemical reactions with the ambient environment over a long period of time. The inner layer of the copper tube surface is mainly made up of a mixture of cuprous and cupric oxides, the predominant one being cuprous oxide. Cuprous oxide can be eliminated by pickling in relatively dilute sulfuric acid solution. Simultaneously, the metal surface is transformed into an activated state, which facilitates the electroless plating process.[8]

Although many procedures have been described as efficient preplating procedures for electroless coatings, no work has been done to compare these cleaning methods, to optimize preplating

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**Table 1 Description of the operating principle of the cleaning agents, the brand names of commercial products, and the main components of cleaning solutions**

| Cleaning agent | Description | Brand name | Main components |
|---|---|---|---|
| Cleaning agent 1 | Solvent cleaner | — | Trichloroethylene |
| Cleaning agent 2 | Solvent cleaner | — | Acetone |
| Cleaning agent 3 | Alkaline cleaner | Deconex | Potassium phosphate, potassium hydroxide, inorganic chlorine, chelating agents, emulsifiers |
| Cleaning agent 4 | Acid cleaner | Hakupur 56/70 | Phosporic acid |
| Cleaning agent 5 | Acid cleaning and activating process, removes oil | Slotoclean BUZ-R | Phosphoric acid, surfactants, deoxidisers, complexing agents |
| Cleaning agent 6 | Alkaline degreaser | Slotoclean AK181 | Sodium hydroxide, complexed phosphate |
| Cleaning agent 7 | Alkaline degreaser | Slotoclean AK181 + VF100 | Sodium hydroxide, complexed phosphate, ionic, nonionic surfactants |
| Cleaning agent 8 | Alkaline degreaser | Emalan 5352 + 0570 | Phosphates, inorganic salts, nonionic emulsifiers, fatty alcohols |
| Cleaning agent 9 | Alkaline emulsion degreaser and anticorrosion treatment | Emulpon 97-10 | Organic salts, nonionic emulsifiers, fatty alcohols, inhibitors |

process parameters, or to address their influence on coating structures and their formation. The objective of our work was to optimize preplating processes by studying the cleaning efficiency of different preplating processes and by demonstrating their influence on the electroless coating buildup.

## 2. Experimental Procedures

### 2.1 Materials and Test Solutions

The object under study was hard-drawn copper tube of size 15 × 1 mm wall thickness. In its production, a commercial synthetic drawing lubricant containing frictional modifiers was utilized to facilitate easier drawing. In contact angle measurements, the device geometry did not allow the use of tubular specimens, and, accordingly, the specimens were plate shaped with a thickness of 0.7 mm and other dimensions of about 30 and 120 mm. Although the form of the samples varied, all were phosphorus-deoxidized copper of the same composition, the phosphorus content ranging from 0.015 to 0.050%. To obtain a real contamination situation for the plate-shaped specimens, the specimens were treated with the same drawing lubricant as used in copper tube production. The excess oil was lightly wiped away from the copper surface to obtain an equal contamination level to tubular specimens. Under the drawing lubricant layer, all the samples had an oxide layer of atmospheric origin.

The experimental work to optimize the preplating process consisted of two parts. First, the cleaning efficiency of different preplating treatments was studied. Emphasis was on the two main stages of the preplating: cleaning and pickling. Second, the entire coating sequence was constructed on the basis of an appropriate preplating process.

In the first part, efficiency of the removal of grease from the copper surface was studied with water-soluble cleaning media of which five were alkaline cleaners and two were acidic. Study was also made of the cleaning efficiency of two solvent cleaners, trichloroethylene and acetone. The main components of the cleaning solutions are presented in Table 1. However, not only the chemistry of the cleaning solution but also the process parameters influence the cleaning efficiency and, accordingly, the properties of the coating. The process parameters of the employed cleaning baths are summarized in Table 2. The oxide layer was eliminated with an oxidizing pickling solution containing approximately 35 g/L sulfuric acid and 0.8 vol.% hydrogen peroxide. The pickling bath was maintained at 40 °C in view of the decomposition of hydrogen peroxide at higher temperatures if no stabilizers are included.[9]

**Table 2 Cleaning bath parameters employed in cleaning studies. Parameters are selected according to the recommendations of manufacturers**

| Cleaning | Cleaning conditions |
|---|---|
| Cleaning agent 1 | Temperature 60 °C, time 5 min |
| Cleaning agent 2 | Room temperature, time 30 s |
| Cleaning agent 3 | Dosage 5%, temperature 60 °C, time 10 min |
| Cleaning agent 3 | Dosage 10%, temperature 60 °C, time 15 min |
| Cleaning agent 4 | Dosage 4%, temperature 60 °C, time 2 min |
| Cleaning agent 5 | Dosage 150 mL/L, temperature 40 °C, time 3 min |
| Cleaning agent 6 | Dosage 4.5 mL/L, temperature 60 °C, time 5 min |
| Cleaning agent 7 | Dosage 1.2 mL/L added to cleaning agent 6, temperature 60 °C, time 5 min |
| Cleaning agent 8 | Phosphate dosage 60 g/L, surface modifier dosage 7 g/L, temperature 40 °C, time 3 min |
| Cleaning agent 9 | Dosage 10 g/L, temperature 60 °C, time 2 min |

% = vol.%

In the second part of the work, the coating structure achieved after different preplating treatments was evaluated. The processing sequence to generate electroless tin coatings on the inner surface of copper tube is illustrated in Fig. 1. The temperature range during the deposition varied from 60 °C to 85 °C. The baths used in the coating process were acidic in nature. The capacity of the solution pump was low in laboratory experiments, while higher solution velocities were reached in production-scale tests. The postplating treatments presented in Fig. 1 are not included in this work.

### 2.2 Surface Cleaning Studies

Measurements to study the cleaning efficiency of test solutions consisted of contact angle measurements in laboratory scale followed by residual oil measurements in production-scale tests. The tests were done only for the most efficient


**Fig. 1** The processing sequence for producing chemical tin coatings

cleaning agents. The laboratory installation consisted of a cleaning vessel (volume about 600 mL) and a contact angle measurement device. A contaminated copper plate was immersed in heated cleaning agent for a specific time, and the cleaning solution was sprinkled on the sample surface with a syringe to simulate the mechanical effect of spraying on the cleaning result. The contact angle measurements were carried out at ambient temperature and in air atmosphere by injecting drops of water and electroless plating solution on cleaned copper surface. About ten droplets were applied with a computer-controlled solution injection system on copper samples purified with each cleaning solution. During injection, the droplet-surface interaction was recorded on video tape with a digital camera and video recorder. The tape was then studied to determine the contact angles of droplets on the copper surface with a special contact angle and surface tension calculation program. The angles were established after 0.5 s of contact. Final contact angle values for cleaned samples consisted of average values calculated from ten measured contact angle values. The production-scale tests utilized residual oil measurements, which is the method normally employed to verify the absence of carbon films on copper tube inner surface in production quality control. The amount of dissolved organic compound residual was determined over a tube length of 180 cm by gravimetric measurement of organics in evaporated cleaning agent according to the standard ASTM B743-85.

The efficiency of the pickling treatment in oxide layer removal was tested by potentiostatic measurements. The potentiostatic measurements were performed using Gamry Instruments Potentiostat (Gamry Instruments, Inc., Warminster, USA)/Galvanostat/ZRA model PC3, and the data were collected with a CMS (Gamry Instruments, Inc., Warminster, USA) 100 electrochemical measurement system. The electrolytic cell utilized in potentiostatic measurements was made of a Duran (Duran glass beakers, Schott Gerate (GmbH, Hofheim, Germany) glass beaker containing copper sample with surface oxide as a working electrode, platinum counterelectrode, and Ag/AgCl containing 3 M KCl as a reference electrode. The area of exposed working electrode was 4.08 $cm^2$. The reference electrode was connected to the test solution *via* a salt bridge in order to bring the electrode in close proximity to the working electrode. Experiments were carried out in pickling solution at 40 °C. In potentiostatic measurements, the potential was kept at the value of $-460$ mV with respect to Ag/AgCl electrode, while the current was measured after every half second during 300 s. The plating sequence was completed before and after the different preplating processes. The sample surfaces were characterized with a scanning electron microscope (SEM) after different deposition sequences. The SEM studies were carried out with a Philips XL30 microscope (Philips Electronics N.V., Eindhoven, The Netherlands).

## 3. Results and Discussion

Figure 2 shows the contact angle values for water and electroless plating solution on contaminated copper. When the oil layer is completely removed, the contact angle measuring medium perfectly wets the substrate. Accordingly, the lower the contact angle the more efficient the cleaning agent and the cleaner the substrate surface for subsequent coating. The results of production-scale residual oil measurements are graphically presented in Fig. 3. The SEM micrographs of coating surfaces after the different preplating processes are presented in Fig. 4.

The solvent cleaners, cleaning agents 1 and 2, exhibited relatively high contact angle values in the case of water injection, and the inefficiency of these cleaners to remove contamination from copper surface was further emphasized when measurements were performed with plating solution. However, the results of residual oil measurements (Fig. 3) clearly indicate that the overall organic drawing lubricant level was dramatically reduced by the trichloroethylene treatment. The detailed surface appearance investigation with the SEM (Fig. 4f) revealed that trichloroethylene is unable to remove the organic soil uniformly from the entire substrate surface, leaving most of the grain boundaries unpurified. The additional carbon layer on the grain boundaries acts as a barrier for the nucleation of coating grains

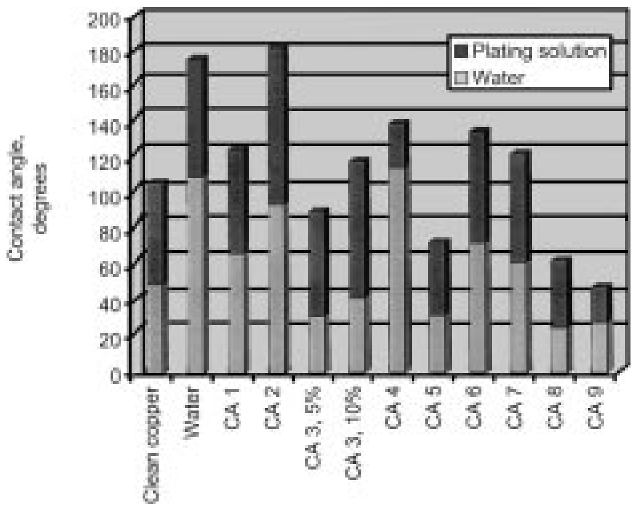



**Fig. 2** Measured contact angle values for water and plating solution on copper samples purified with different cleaning solutions. Clean copper in figure is uncontaminated copper, water stands for contaminated copper cleaned only with water, and CA denotes the various cleaning agents

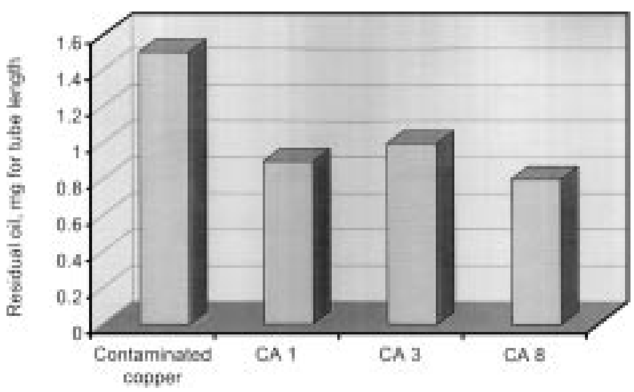



**Fig. 3** Amount of residual oil for contaminated copper and copper samples purified with selected cleaning agents

leading to discontinuous coating structure. Subsequently, coating nucleates inside the grains with no deposit on grain boundaries. Tin grain growth inside the coating is also somewhat restricted by the carbon residuals as a result of poor cleaning capacity. Grain boundaries act as discontinuities in the coating, being easily accessible for plating solution. This results in the formation of tin coating tubercles on grain edges. Such irregular coating formation gives rise to the poor adhesion properties of the subsequent tin coating. Reduced adhesion owing to poor cleaning is in agreement with earlier observations[4] with electroless nickel deposits.

The highest contact angle value for water on copper was observed for phosphoric acid-based cleaning agent 4. The value was even larger than that for water-purified substrate, which illustrates the pronounced polar nature of phosphoric acid bath. In contrast, when surfactants and complexing agents were added to phosphoric acid-based cleaning solution, cleaning agent 5, the behavior of water in contact with the cleaned copper altered dramatically. Cleaning agent 5 had one of the lowest contact angle values among the samples measured with water. The general trend in the wetting behavior was not changed when the injected water was replaced with plating solution. In visual examination, cleaning agent 5 was found to yield a very bright and clean copper surface after cleaning. Still, as much as the good cleaning efficiency makes cleaning medium 5 an attractive choice for optimal surface treatment before electroless coating, its high cost (over fivefold that of alkaline cleaners) rules out its use for large-scale cleaning purposes.

Among the alkaline degreasers, sodium hydroxide-containing cleaners 6 and 7 exhibited the highest contact angle values, while the alkaline cleaning agents containing phosphates (cleaning agents 3 and 8) exhibited more effective wetting. The absence of surfactants in cleaning agent 6 gave it poorer wetting than cleaner 7, which contained surface active agents. The good wetting performance of alkaline cleaning agents 3 and 8 was supported by the visual study of the copper surface after cleaning. These solutions were discovered to leave the copper surface very bright and clean after degreasing. The results of residual oil measurements (Fig. 3) indicate that the surface modifiers added to cleaner 8 not only give it a low contact angle value but also an ability to efficiently remove the oily contaminant from the substrate surface. Simultaneously, cleaning agent 3 was confirmed not to clean the copper surface effectively enough. This is also evident from SEM examinations (Fig. 4b), where coating nucleation is restricted by organic residues. Contact angle values for the alkaline emulsion cleaner 9 appeared to be rather small, but the foaming of this cleaner during spraying decreased its practical usefulness in the tube inner surface treatment. This is in agreement with the visual examination of the copper surface treated with cleaning agent 9, since the surface was rather oily despite the low contact angle values.

As for alkaline cleaners, a too powerful cleaning process may lead to an increased tendency for oxide formation on the copper surface. This is consistent with thermodynamic considerations.[10] Although the manufacturer's recommendations concerning the cleaning solution dosage and the treatment parameters were strictly followed, oxide layer buildup was evident for alkaline degreasers 3 and 6. Oxide layer formation restricts the accessibility of rinsing solution on the pure copper surface, leading to higher contact angle values. Also, tin coating nucleation is hindered. Figure 4(c) illustrates the influence of the cuprous oxide layer on tin deposit formation. The oxidized areas show no tin deposit, while the oxide-free areas are coated normally, enhancing the tin tubercle development on the brinks of deposit.

Figure 4(a) represents the tin coating structure after successful cleaning procedure with cleaning agent 8. Tin coating nucleated uniformly over the entire surface leading to good adhesion properties. The surface roughness (Fig. 4a) and some variations in tin grain size are due to the drawing flutes, which play an important role in the accessibility of the plating solution to different areas of the substrate surface. Still, tin grains wholly and densely cover the copper surface supporting the earlier evidence of the efficiency of cleaning agent 8.

If rinsing is poor, the residues of surfactants and surface modifiers originating from cleaning solutions remain on the copper surface. Surface active agents operate as leveling agents

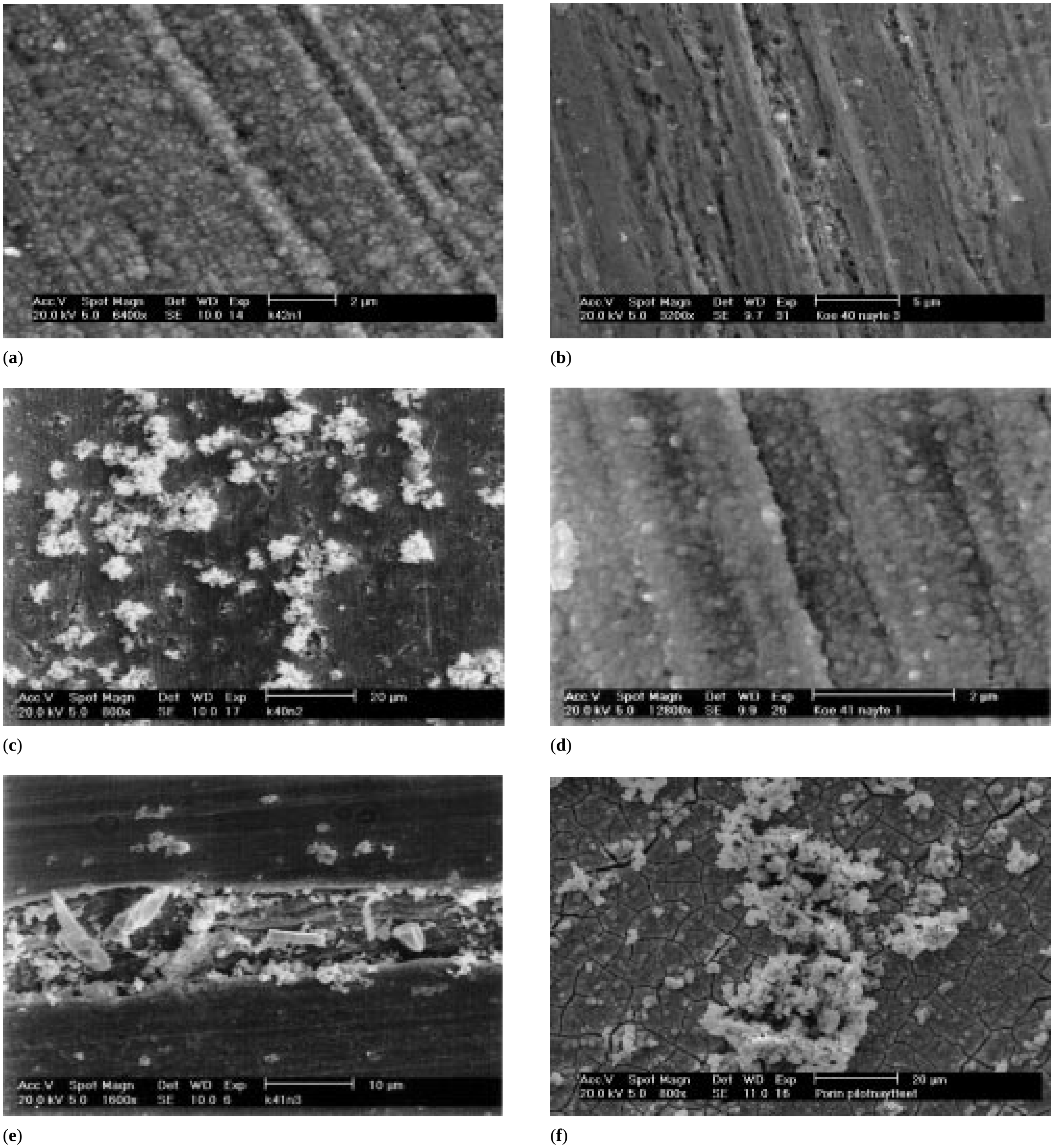



**Fig. 4** SEM images of electroless tin coating surfaces after different cleaning procedures. (**a**) Cleaning carried out by cleaning agent 8, magnification 6400×; (**b**) cleaning performed with cleaning agent 3, magnification 3200×; (**c**) tin coating on oxidized copper, magnification 800×; (**d**) tin coating after poor rinsing of cleaning agent 8, magnification 12,800×; (**e**) the role of drawing flutes on tin coating nucleation in the case of poor rinsing, magnification 1600×; and (**f**) tin coating deposited on copper surface degreased with cleaning agent 1, magnification 800×

serving as nucleating sites for tin grains, but simultaneously hindering the further growth of grains (Fig. 4d). This leads to smooth but very thin tin coatings provided that the surfactant residues are homogeneously distributed. However, surface irregularities, pores, and flaws tend to be difficult to reach by the rinsing solution. The role of the drawing flute on tin nucleation and growth is illustrated in Fig. 4(e). Tin grains nucleate on the sharp edges and the projections of the drawing flute, since these are the areas of more efficient rinsing. The deposit around the surface irregularities was found to be poorly adherent to copper substrate, which is consistent with earlier findings regarding the electrochemical coating characteristics of contaminated substrate.[12]

The success of the pickling process on the copper surface is controlled by two mechanisms: the selective etching of copper grain boundaries at too short pickling times and the pronounced localized corrosion during too powerful pickling treatments. The first mechanism may lead to a discriminative tin deposition mainly on grain boundaries and on some localized areas of thinner oxide layer and the second to an uneven coating finish due to surface pits.

Figure 5 illustrates the monitoring of pickling evolution on atmospherically oxidized copper by potentiostatic measurement. The time for successful oxide layer removal was 6 s. This is consistent with earlier suggestions[4] recommending pickling times of 15 to 300 s depending on the size of the area under exposure. Accordingly, in laboratory and pilot-scale coating routes, where longer copper tubes with greater revealed area were coated, pickling times from 180 to 240 s were utilized. These values were determined experimentally, but calculations from potentiostatic measurements support them. However, the

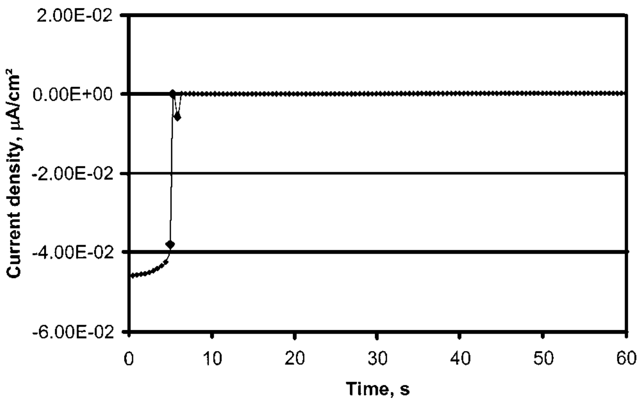
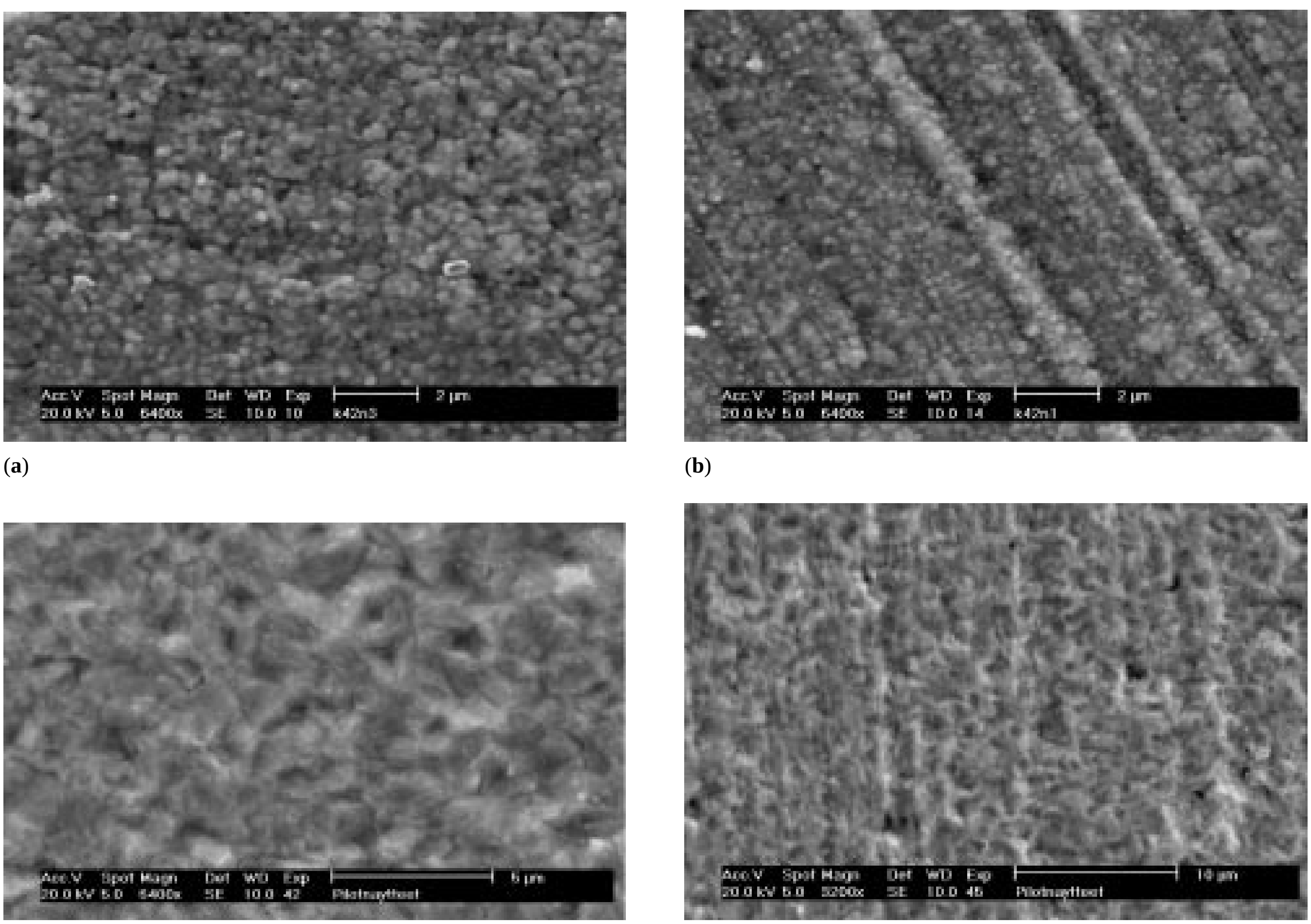



**Fig. 5** The most informative measuring data from the potentiostatic monitoring of oxide layer removal



(**a**) (**b**) (**c**) (**d**)

**Fig. 6** SEM images of electroless tin coatings on copper substrate cleaned with cleaning agent 8 after different pickling and plating sequences. (**a**) Coating deposited after successful pickling and at slow plating solution circulation rate, magnification 6400×; (**b**) coating deposited at slow plating solution circulation rate, no pickling, magnification 6400×; (**c**) coating deposited after successful pickling and at faster plating solution circulation rate, magnification 6400×; and (**d**) coating deposited at faster plating solution circulation rate, no pickling, magnification 3200×

time required to make the copper surface oxide free is always dependent on the oxide layer thickness, and for heavier oxide layers formed, for example, by thermal exposure, longer pickling times are needed.

The microstructures of tin coatings after different pickling and plating sequences are illustrated in Fig. 6. The influence of pickling on the electroless tin coating structure was dramatic, as coating smoothness was radically increased by pickling. Pickling evidently serves to extract the substrate surface roughness and, thus, to eliminate the role of drawing flutes in coating formation. Besides, the surface is simultaneously activated. This activation gives rise to tin grains of equal size in the entire coating structure, in contrast to coating at the unpickled surface where the grain size varied widely. Although Iacovangelo and Zarnoch[12] have reported the important role of oxide layer elimination in electroless tin coating adherence, this was not observed in our study, probably due to our use of extremely powerful degreasing agents to purify the copper surface. Still, their suggestions concerning the brightly colored surface finish after successful pickling and the smoother coatings associated with oxide-containing substrates seem to be prevalent. Moreover, not as much the pickling procedure as the coating solution velocity seems to affect the coating porosity with denser deposit formation obtained at an increasing solution flow rate.

## 4. Conclusions

The present study reports observations on preplating process optimization and on the role of degreasing and pickling treatments in the electroless tin coating buildup on the copper tube inner surface. The following conclusions can be drawn.

- Organic drawing lubricants can be effectively removed from copper substrate surface with alkaline degreasers, of which those containing phosphates are the most efficient. Oil removal from the copper surface by conventional trichloroethylene degreasing is neither appropriate in these days of developed surface technology nor efficient enough for subsequent electroless plating. The use of acidic cleaning agents for surface cleaning is too costly to be commissioned in larger scale.
- Too weak cleaning efficiency of degreaser leads to hindered nucleation and growth of tin coating. In areas of easier solution accessibility, tin grain tubercles may form due to the uneven surface condition. Also, the coating adherence to substrate suffers.
- Adequate rinsing after degreasing is of great importance. A dramatic change in electroless tin coating buildup occurs if degreaser residuals remain on the substrate surface. As a result, surface modifiers in the cleaner act as leveling agents in the coating formation, thus interfering with the deposit growth.
- Successful pickling is controlled by the selective etching of grain boundaries and localized corrosion, which take place with too weak and too powerful pickling procedures, respectively. Completely oxide-free copper surface results in an even and uniform tin coating structure with pleasing deposit appearance.
- Contact angle measurement is suggested to be a versatile tool for comparing the efficiencies of different surface cleaning treatments. The use of water and electroless plating solution as measuring media reflects the ability of water to rinse the overall surface and the behavior of the plating solution in the areas of difficult accessibility of the rinsing solution, respectively.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