Effects of New Additives (Lanolin) on the Electro-Deposition of Copper Powder

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Abstract
New organic compound (Lanolin) is added to the electrolyte of copper powder deposition unit. The influences of the copper concentration, current density, and specific surface on the apparent density of the produced powder had been studied. Also the mean grain size of powder, mass of deposited powder are been calculated. The best concentration of lanolin is 0.7% at which grain size deposits are smooth and fine (about 93% less than 53 micron) and had high purity of 99.9%.

Keywords: Lanolin, copper powder, electro-deposition, electrolysis, current efficiency, apparent density

Introduction
The powder is defined as a finely divided solid, smaller than 1000µm in its maximum dimension. A particle is defined as the smallest unit of a powder. The particles of many metal powders are 25 to 200 µm in size (1). The industrial output of copper powder is greater than that of any other metal powder (2-4). This can be attributed to a wide range of using copper and copper alloys powders in an industrial applications. Pure copper powder is used in the electrical and electronics industries because of its excellent electrical and thermal conductivities. The applications of copper powders are quite extensive. They are used in typical applications like:
- Piping-computer chips-paints, coatings, inks, plastic-metal combinations brazing pastes.
- Alternator brushes.-catalyst applications, Friction components, Chemical formulations, medicine.

They are used to do things like study brain function and treat cancer and another health application is copper kills many bacteria.

Copper powder can be produced by number of methods, the most

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important are: atomization, electrolysis, hydrometallurguy and solid state reduction. Each method yields a powder having certain inherent characteristics. Table 1 Indicates considerable variation in properties can be obtained by various types of powders.

Electrolysis is the most economical method; moreover the copper powder obtained is of the highest quality. Electrolytic powder is produced from high purity cathode copper and the powder is consistently more than 99% pure. Copper deposition occurs when an electrical potential is established between the anodes and the cathodes. The ions will migrate, the positively charged ions towards the cathode, or the negatively charged ions towards the anode or positive electrode. When current passes through the copper plate, the last dissolves according to the following equation:

\[
\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu (copper atom)}
\]

These copper atoms, then add on to the crystallographic powder on the electrode surface.

Dissolution of copper and copper ions discharge processes occur at lower potentials than that of other possible reactions. If the applied potential is increased, the rate at which copper ions are discharged increases, eventually the rise in potential, however, other reactions occur, the most important of which is the discharge of hydrogen ions to give hydrogen evolution:

\[
\text{H}^+ + e^- \rightarrow \text{H}_2 \text{(hydrogen atom)}
\]

Also oxygen evolution can take place as following equation:

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

Sulphate ions (SO\textsuperscript{4}=), which are also attracted to the anode do not usually discharge, for the potential at which occurs is high, higher than those potentials commonly used in electrodeposition. The electrodeposition process affected by solution concentrations, which affects the electrolysis. Electrolysis conditions favoring diffusion control to enhance formation of the electrolytic metal powder. For example, decreasing metal salt concentration, increase of concentration of indifferent electrolyte, decrease of stirring rate, increase of current density.

\[
\text{An} + \text{C} = \text{Cu}_{\text{amorphous}} + \text{C}
\]

The powder has a tendency to form flakes or needles, fibrous or spongy forms, etc., depending on the electrodeposition process parameters and on the nature of the metal. The shape and size of powder particles depend also on the kinetic parameters.
of the deposition process \(^{(1, 4, 7)}\). If the kinetics of the deposition process is fast powder can be obtained at low driving force, while a much larger driving force is needed for kinetically slow processes \(^{(4)}\). The apparent density, the flowability, and the specific surface are the most important properties of metal powders \(^{(2, 3)}\), but in practice the quality of the powder is mostly determined by the apparent density \(^{(2)}\).

Electrolytic copper powder consists of particles, whose dimensions & forms are more suitable for practical applications than powders obtained in other ways \(^{(5)}\) because of its high purity, is particularly suited for P/M components in the electronic and electrical industries where high electrical and thermal conductivities are required \(^{(8)}\). However, it is suitable for self lubricating bearing, alloying with tin, zinc, nickel and other elements to form brasses, bronzes and other copper alloys. Also copper and copper alloys powder are used in such non structural applications as brazing, cold soldering and plating as well as for medals and medallions, metal plastic decorative products and other P/M applications \(^{(6)}\).

Some researchers \(^{(6)}\) had investigated systematically the influences of various additives on deposition of copper powder. As additives they employed glucose, glycerin, glue, gelatin and others. Some of these additives exert little (and other high) influence on the formation of powdery copper electrolytic deposits. Most of additives modify to some extent the current efficiency. For an additive concentration of 0.1% maximum current efficiencies are obtained and volumetric mass which accompanies the increase of specific surface is decreased. Some additives sensibly enlarge the volumetric mass of the copper powder. This work aims to study the influences of new additives (lanolin) on the copper concentration, current density, specific surface, apparent density and mean grain size of powder.

**Experimental Work**

**Apparatus**
The apparatus used in this work consists mainly of

1. **The electrolytic cell**
   This cell is an open tank, which made of (PVC) plastic. Inner dimensions of the cell are \((42 \times 15 \times 20)\) cm. The cell has a slanting bottom, so that the deposited powder can easily move to a specific place for removal. The cell is equipped with three anodic electrodes and two cathodic electrodes. Each electrode is rectangular copper flat plate with dimensions \((10 \times 4)\) cm and \(0.9\) cm thickness. The electrodes are positioned as parallel plates with inner spacing \(2.5\) cm. The electrodes are cited \((5\) cm\) a above the cell bottom. The anodes and cathodes are connected to the \((+)\) & \((-)\) current lines of powder supply respectively. Figure 1 shows the structure of the used cell.

2. **Aqueous solution**
   The process for electrolytic powder deposition is carried out in aqueous solution, which contains \(0.7\) molar copper sulfate, \(2\) molar sulfuric acid. New organic additive are used as secondary compound. This compound is Lanoline (or lanum). The effective lanoline concentrations used were \(0.35\%\), \(0.45\%\), \(0.7\%\) and \(1\%\). Lanoline is an organic compound, recovering from scouring of wool. It is wool grease or wool wax. It has unusual property of forming stable semisolid
emulsion, containing up to 80% water.

There have been no researches concerned with the identification of these new organic additions. Therefore, this research is the first work in which Lanoline was used in the process of electrolytic copper powder deposition.

3- Power supply (type poli power struers) of 15 A and 50 volts was used.
4- Electrical mixer (type Hettler STI) with 100-1000 r.p.m. was used.
5- Standard sieves of specific number

The separation of powder into particle size ranges achieved by using of series of graded typical sieves. Practical size distribution expressed as the weight percentage retained upon each of a series of standard sieves of decreasing size and the percentage passed by the sieve of finest size. The percentage by weight into which a powder sample has been classified with respect to sieve number or microns.

The common particle size callout is a mesh count. This refers to the number of openings per inch in a mesh used to sift the powder. The higher the mesh count, the smaller the particle size.

5- Cylindrical container

Apparent density – The weight of a unit volume of powder, usually expressed as grams per cubic centimeter, determined by letting the powder drop freely through a funnel to fill a 25 cm³ Cylindrical container.

6- Permeameter type Lea and Nurse Instrument

The specific surface- The surface area of one gram of powder, usually expressed in square centimeters. The specific surface of metal powders is measured with permeameter-like devices type Lea (Nurse Instrument), Blaine permeameter and the universally adopted Fischer sub sieve seize, and for very fine powders the gas adsorption method is adopted (BET method).

Sub sieve Fraction – Particles all of which will pass through a 44 micron (No. 325) standard sieve.

Super fines – The portion of a powder composed of particles that are smaller than a specified size, currently less than 10 microns.

7-Simple Filters

The electrolyte powders are filtrated and then washing with dilute sulphuric acid until the powder is free from copper ions. Hot water washing follows until (SO₄)²⁻ ions are completely removed.

The elements which are more noble than Cu and the compounds are anodically insoluble and precipitate on the bottom of the cells beneath the anodes as ‘anodic slimes’ or ‘anodic sludge’. The sludge removed by filtration of the electrolyte, although in some cases (e.g. Pb) the sludge collects on the anode which periodically removed from the cell and scraped.

8- Auger Electron Spectroscopy

In this work, electron induced Auger electron spectroscopy (in laboratories of petroleum ministry) is used to measure the specific surface area of powder.
Operation condition

The unit of electrolyte deposition in this work yields 0.5 kg of copper powder under following operation condition:

1. Temperature is maintained below 40 °C. This was achieved in this work by continuous circulation of the electrolyte. Circulation rates are typically 0.01-0.03 m³/min.

2. The terminal voltage range is 1.2-2.0 volts, depending on the conditions of the process.

3. The anodic and cathodic current densities are 4.5 Ampere/dm² and 30 Ampere/dm² respectively.

4. A cell is achieving a nominal change of electrolyte every 4-6 hrs.

5. Powder is removed from cathodes by manually shaking (a brushing) every 15-20 minutes intervals.

Washing & Drying of Copper Powder

Powder accumulated at the bottom of the cell is decanted and washed with water to separate it from the electrolyte. The wet powder is then treated with a dilute solution of 0.05% Na₂CO₃ to remove traces of acid. The carbonate excess is washed off with water several times. The powder is finally washed with 6 g/l solution of sodium and potassium tartrate, which act as anti-oxidation during drying. Drying is carried out in vacuum furnace at 150 °C. The powder is then stored in a dry atmosphere.

Results and Discussion

Polarization curve for the potentiostatic deposition of copper can be used to explain the dependence of electrolytic copper deposition process on electrochemical parameters (9, 10).

Figure 2 illustrates the dependence of current on electrode potential for copper deposition in aqueous solution, which contains 0.7 molar copper sulfate, 2 molar sulfuric acid and 0.7 % new organic additive Lanoline (or lanum). As shown from (Figure 2) electrodeposits obtained in different overpotential ranges. There are three ranges clearly visible on the polarization curve according to deposit powder:

(a) Compact metal, (b) rough deposit, and (c) true powder.

At very low overpotential, the depositions of powders practically are not detected. Hence, powder nucleus formation overpotential is not a prerequisite for the initiation and growth. It can be stated that, compact deposits form in condition which, allow the discharge and incorporation of hydrogen into deposited metal. In the first range, the current increases with overpotential increases. The transition from compact to rough deposit occurs, when the current increases with overpotential increases.

Current until the current takes constant value although the overpotential increases. The constant current value indicates to limiting diffusion current. Some researchers (6,7) admitted that, overpotential determines the degree of supersaturation at which electrodeposition of copper powder...
occurs and supersaturation is the driving force of crystallization and determines the pathway of the process.

The rough deposit range begins at more noble potentials ( +250 V ), when dissolution rate decrease to a very small value and the current observed to be initially independent on potential as shown in figure 2. It has been shown that, the limiting currents cover a wide range of potential in rough deposit stage.

These results show clearly that a distinction has to be made between rough and powdery deposits. The results emphasis that, the copper deposition process is a function of electrode potential. The potential of powder formation are larger than those corresponding to the beginning of limiting current and powdery deposit forms in the range of limiting current value, at overpotential / current density values larger than the critical values, as illustrated by Figure 2.

Hence, in potentiostatic (constant potential) electrodeposition of powders, the overpotential must be larger than the overpotential corresponding to the end of the limiting diffusion current density plateau (5). At very noble potentials (+650 V), dissolution rate again increases with increasing potential. The criterion for obtaining powdery deposits is that the electrode process must be controlled by the diffusion of ions to the electrode surface, rather than the kinetics of the electrodeposition(5,7). 

The electrolyte additionally contains organic additives of lanolin, which serve to control copper electrocrystallization at the cathode (serve to regulate and distribute the delivery of copper deposition insoluble particulates from co-deposition (surfactants process) and help prevent). The (Lanolin) works within the film layer to control copper deposition on a microscopic level. It tends to be attracted to points of high electro-potential, temporarily packing the area and forcing copper to deposit elsewhere. As soon as the deposit levels, the local point of high potential disappears and the (Lanolin) drifts away. (I.e. Lanolin inhibit the normal tendency of the deposition bath to preferentially plate areas of high potential which would inevitably result in rough, dull deposition) By continuously moving with the highest potential, Lanolin prevents the formation of large copper crystals, giving the highest possible packing density of small equiaxed crystals. 

Table 2. Shows the influences of various concentrations of Lanolin (0.35%, 0.45%, 0.7% and 0.7%) on characteristics of copper powder deposition. The results indicate that, the low concentrations exert little influence on the powder formation while for an additive concentration of 0.7% maximum powder, which have less than 53µm finesse are obtained. These concentrations also modify to some extent the apparent density of the produced powder. However, addition of lanolin causes a marked increase of weight percentage of deposited powder with high purity and decrease of main grain sizes. Hence, it can be seen from the data in Table 2 that in order to obtain pure metals at the cathode, the current density is always low.

The lanolin is assumed to mark possible the deposition of extremely fine powder and to diminish the
discharge of hydrogen at the cathodes.

When the lanolin concentration exceeds the 0.7% to 1%, the mass of deposited powder less than 53 µm and current efficiency decrease from 93.2, 69 to 91 and 66.4 respectively. Therefore 0.7%. Lanolin will be dependent in the further experiments.

The most significant recent development in copper deposition which obtained when lanolin is added has been copper assay (99.9%) and the percentage of powder less than 53 finesse is (93.2%) as shown in Table 2.

Best conditions of periodic current reversal permit cathode current densities of up to 36 mA/cm². The preferred ratio of forward-current time: reverse-current time is 20 or 30 to 1, with identical forward and reverse currents, for a cycle time of 0.5-3 min. Optimum working conditions when lanolin was added observed in Table 4.

The dependence of the apparent density on copper ion concentration is illustrated by Figure 3. This figure gives well evidence that with increase copper ion concentration (with or without lanolin) the apparent density of getting powder increases also but the rate of increase, when lanolin add is larger than that without lanolin.

Figure 3. indicated, that when 0.7% lanolin add, the apparent density is higher than that with out lanolin (curve 2 % curve 1). This can be attributed to increase the volumetric mass as lanolin is existed.

Copper ion concentration is very necessary to powdery deposit[4,6] because if deposition of copper (at the cathode) and dissolution of copper (at the anode) both proceed at 100 per cent efficiency, the total copper ions content of the electrolyte will remain constant, but if the rate of copper deposition larger than dissolution rate, the solution in the vicinity of the cathode will become depleted in copper ions, therefore the increase of copper ion concentrations means increase of both dissolution of copper at anode and deposition of copper ions on the cathode[4,7].

The current density in this process strongly influences the deposition[8]. This current density can vary with or with out addition of lanolin. When 0.7% lanolin adds, it will tend to have a higher current density than that without addition as shown in figure 4. The higher current density (in case of lanolin) refers to faster depositing rate of copper powder and the deposited powder have poor adhesion with the cathodic surfaces. This made the removal powder process very easy. Figure 4. Illustrates that when 0.7% lanolin is used the relationships between current density and apparent density will be organized and becomes linear.

From experimental stand point, the true powdery deposits are of two kinds, some are formed at low current density and other, the most characteristic are disperse deposits formed at high current density.

At low current density, the powdery deposits are spongy, bulky and soft. The conditions which favor the formation of spongy deposits are: high sulphuric acid concentration, low copper ion concentration, and low lanolin concentration.

At high current density, copper powder form in the range of the limiting diffusion current[2,7]. At a certain current density, the powder separates, at first as a compact deposit; this after 2 hours turns
powdery. The powdery deposits are the most important kind of disperse deposits \(^8\). They represent an accumulation of particles whose dimensions depend on the conditions of formation. They have generally red color.

It is possible to plot the dependence of apparent density on the specific surface copper powder as can be seen from Fig. 9. The larger is the specific surface the lower is the apparent density. The specific surface area of powder depends on the electrolysis parameters \(^3, 9\); particularly on the medium from which deposition takes place. In media with 0.7% lanolin (as shown in figure 5), the particles powder have low specific surface, when the apparent density of the powder reached max. Value and as the specific surface increases the apparent density decreases while the apparent density becomes independence on the specific surface at specific surface large than 200 \(\text{cm}^2/\text{g}\).

The electrolytic metal powder is not formed of particles of identical size and morphology; the individual particles may assume various form and sizes, while the powders as associations of such particles exhibit, more or less, the same characteristics if are deposited under the identical conditions\(^1, 4\). Typical particle-size distribution curves for copper powders obtained at addition of lanolin and without lanolin are shown in Figure 6. It is observed from Figures 6, that the weight per cent of produced powder increases and the mean particle-size of powder decreases when 0.7% lanolin was been added, and that particle-size distribution curve is sharp. The 149-177 mA/cm\(^2\) fraction of powder obtained at 0.18 A/cm\(^2\), exhibit excellent flowability while the non-sieved powder shown in Figure 6 does not flow. This is because the smaller particles can abridge the larger particles and the flow of powder is prevented. Hence, the surface structure of a non-sieved powder with good flowability must be more compact and smooth. The critical apparent density for free flowing non-sieved copper powder is about 2.2-2.3 g/cm\(^3\). Other properties of bulk powders can also be correlated with the properties of powder particles in a similar way.

Current density also affects grain size as proved above (Figure 3) when the lanolin was added the current density will be higher than that with out lanolin therefore grain size deposits are smooth and fine.

Conclusions
1- The influences of various concentrations of Lanolin (0.35%, 0.45%, 0.7% and 0.7%) on characteristics of copper powder deposition. The results indicate that, the low concentrations exert little influence on the powder formation while for an additive concentration of 0.7% maximum, the weight per cent of produced powder with high purity increases and the mean particle-size of powder decreases. When the lanolin concentration exceeds the 0.7% to 1%, the weight percentage of deposited powder and current efficiency decrease from 93.2, 69 to 91 and 66.4 respectively. Therefore 0.7%. Lanolin will de dependent as the best concentration in the this work.

2-In aqueous solution, which contains 0.7 molar copper sulfate, 2 molar sulfuric acid and 0.7 % new organic additive Lanoline (or lanum),
there are three ranges clearly visible on the polarization curve according to deposit powder:

(a) Compact metal, (b) rough deposit, and (c) true powder. Powdery deposit forms in the range of limiting current value, at overpotential / current density values larger than the critical values.

3- The most significant recent development in this work is obtained powders, when lanolin is added, had copper assay (99.9%) and the percentage of powder less than 53 finesse is (93.2%).

4- The dependence of the apparent density on copper ion concentration gives well evidence that with increase copper ion concentration (with or without lanolin) the apparent density of getting powder increases also but the rate of increase, when lanolin add is larger than that without lanolin.

5- When 0.7% lanolin is used the relationships between current density and apparent density will be organized and becomes linear. The current density is high in case of lanolin, which refers to the deposited powders had poor adhesion with the cathodic surfaces and the depositing rate of copper powder was fast. This made the removal powder process very easy.

6- In media with 0.7% lanolin, when the apparent density of the powder reached maximum value, the particles powder had low specific surface and as the specific surface increases the apparent density decreases while at specific surface large than 200 cm²/g, the apparent density became independence on the specific surface.

References


Table 1. Typical Properties of Copper Powder Produced by Various Methods

<table>
<thead>
<tr>
<th>method</th>
<th>Atomization</th>
<th>Electrolysis</th>
<th>Hydro-metallurgy</th>
<th>Solid State Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper %</td>
<td>99-99.5</td>
<td>99-99.5</td>
<td>99-99.5</td>
<td>98-99</td>
</tr>
<tr>
<td>Weight Loss in H₂ %</td>
<td>0.1-0.75</td>
<td>0.1-0.75</td>
<td>0.1-0.75</td>
<td>0.1-0.75</td>
</tr>
<tr>
<td>Acid Insoluble %</td>
<td>0.5-0.1 max</td>
<td>0.03 max</td>
<td>0.03 max</td>
<td>0.3 max</td>
</tr>
<tr>
<td>Apparent Density g/cm³</td>
<td>2-4</td>
<td>1.5-4</td>
<td>1.5-2.5</td>
<td>2-4</td>
</tr>
<tr>
<td>Flow, sec/50 g</td>
<td>20-35</td>
<td>30-40</td>
<td>none</td>
<td>20-35</td>
</tr>
<tr>
<td>Green Strength psi</td>
<td>2500 max</td>
<td>400-6000</td>
<td>10,000 max</td>
<td>2500 max</td>
</tr>
<tr>
<td>MPa</td>
<td>17.2 max</td>
<td>2.8-41.3</td>
<td>68.9 max</td>
<td>17.2 max</td>
</tr>
<tr>
<td>-325 mesh %</td>
<td>25-80</td>
<td>5-90</td>
<td>60-95</td>
<td>25-50</td>
</tr>
</tbody>
</table>
Table 2. Shows the influences of (Lanolin) in the finesse of produced copper powder and in the current density and the mass of deposited powder.

<table>
<thead>
<tr>
<th>Con. of Lanolin %</th>
<th>0</th>
<th>0.035</th>
<th>0.045</th>
<th>0.07</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average current (A)</td>
<td>4</td>
<td>4.35</td>
<td>4.2</td>
<td>3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Mass of deposited powder gm (theoretically)</td>
<td>31.6</td>
<td>34.37</td>
<td>33.18</td>
<td>30</td>
<td>27.6</td>
</tr>
<tr>
<td>Mass of deposited powder (practically)</td>
<td>22.9</td>
<td>25.4</td>
<td>24.2</td>
<td>20.7</td>
<td>18.36</td>
</tr>
<tr>
<td>Mass of deposited powder less than 53 µm (practically)</td>
<td>20</td>
<td>23</td>
<td>22.3</td>
<td>19.3</td>
<td>16.7</td>
</tr>
<tr>
<td>Current efficiency %</td>
<td>72.3</td>
<td>74</td>
<td>73</td>
<td>69</td>
<td>66.4</td>
</tr>
<tr>
<td>The percentage of powder less than 53 finesse</td>
<td>87.3</td>
<td>90.5</td>
<td>92.2</td>
<td>93.2</td>
<td>91</td>
</tr>
</tbody>
</table>

Table 3. Chemical composition of produced copper powder

<table>
<thead>
<tr>
<th>Element</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>0.025</td>
</tr>
<tr>
<td>Al</td>
<td>0.04</td>
</tr>
<tr>
<td>Mn</td>
<td>0.005</td>
</tr>
<tr>
<td>Cu Assay</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Table 4 Best Working conditions when lanolin was added

<table>
<thead>
<tr>
<th>Distance between electrodes</th>
<th>2.5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of electrodes</td>
<td>5 (Three anodes and two cathodes)</td>
</tr>
<tr>
<td>Time for passage current</td>
<td>100 min.</td>
</tr>
<tr>
<td>Con. Of sodium sulphate</td>
<td>50 gm/l</td>
</tr>
<tr>
<td>Speed of revolution</td>
<td>200 r.p.m</td>
</tr>
<tr>
<td>Con. Of sulfuric acid</td>
<td>150</td>
</tr>
<tr>
<td>Con. Of copper sulphate</td>
<td>25</td>
</tr>
<tr>
<td>Temperature</td>
<td>30 C</td>
</tr>
<tr>
<td>Total voltage</td>
<td>1.6 V</td>
</tr>
</tbody>
</table>
Figure 1. An electrolytic cell for the deposition of copper powder

Figure 2. Polarization curve for the potentiostatic deposition of copper in aqueous solution, which contains 0.7 molar copper sulfate, 2 molar sulfuric acid and 0.7% new organic additive Lanolin.

(a) Overpotential: 200 mV, 
(b) Overpotential: 300 mV, 
(c) Overpotential: 700 mV, deposition time: 2 min.
Figure 3. The effect of copper ion on the apparent density:
--- Series 1 without Lanolin     --- Series 2 with 0.7% Lanolin

Figure 4. The effect of current density on the apparent density:
--- Series 1 without Lanolin     --- Series 2 with 0.7% Lanolin
**Fig. 5.** The apparent density of copper powder as a function of specific surface powder which deposited by using addition of 0.7% lanolin.

**Fig. 6.** Mean size of deposited copper powder without Lanolin (Series 1) and with Lanolin (Series 2).