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Technical and economic advantages of making lead−acid battery grids by continuous electroforming

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Abstract

A new continuous electroforming process to manufacture lead grids for automotive and industrial lead−acid batteries has been developed. A galvanic cell comprising a drum cathode for electroforming and a subsequent series of galvanic cells which form a strip galvanizing line are operating in a single, fully continuous, automatic process. Virgin lead or lead scrap may be used as the anode material.

The product is grid strip of any specified thickness and design which can be fed into existing strip-pasting equipment. The composition and microstructure of the grid material can be varied to provide increased corrosion resistance and increased paste adherence. A unique feature of the material is its inherent layered composite structure that allows optimization of the properties according to particular functional requirements. Thus, both the specific power and the specific energy of the battery can be increased by reducing weight. The material properties increase the calendar life of the battery by increasing the corrosion resistance of the grid, and increase the cycle-life of the battery by improved adherence of the positive active material.

The technical and economic features and competitive advantages of this new technology and product are presented in quantitative terms.

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1. Introduction

The established technologies of grid making for lead–acid batteries, i.e. book-mould casting, strip expanding, and strip stamping, are inherently limited as to the extent to which the grid design, microstructure, and properties can be optimized independently of the restrictions imposed by the process. A new alternative technology of grid production by continuous electroforming is overcoming these limitations to a large measure. The technology is advantageous technically as well as economically. In this study, both aspects are treated in quantitative terms.

Previous accounts of the new technology have essentially described its principal features [1–4]. In the meantime, the process has been implemented in a fully-automated pilot line that is presently used to optimize the process variables and to produce test grids. The test results and model calculations reported here are based on the authors' own work

as well as on external investigations of electroformed grid specimens.

2. Experimental

The principle of the continuous electrodeposition process is shown in Fig. 1. The cathode in the first cell, on which the electroforming of the grid strip takes place, is a cylinder with a surface that is patterned into conductive and non-conductive areas according to the desired grid design. While the cylinder revolves at a predetermined rate, an initial grid strip is deposited on to the conductive parts of the surface. The strip is about 50–150 μm in thickness. The deposit is stripped continuously from the cylinder surface. This thin grid strip is then immediately passed through a galvanizing line. The line consists of several cells in which the strip is plated further until it has reached a specified thickness, typically in the range of 0.4–2 mm. In the pilot equipment, which is shown in Fig. 2, grid strip is formed continuously according to the principle shown in Fig. 1. It is comprised of the electroforming cylinder cell and one strip galvanizing cell. This equipment has been constructed according to a

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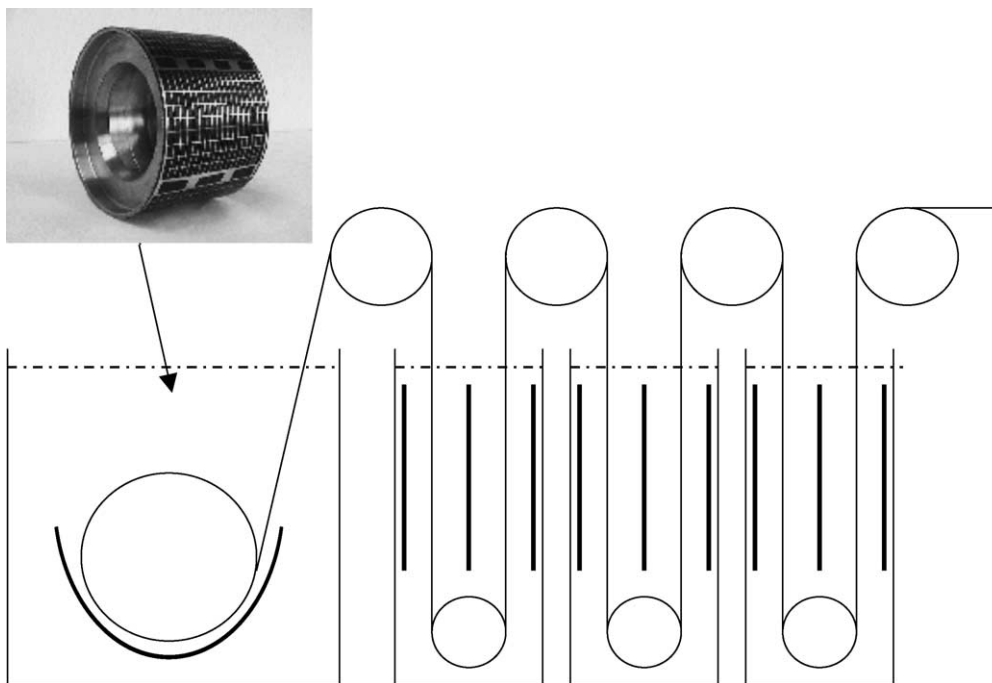*E-mail address:* warlimont@ifw-dresden.de (H. Warlimont).

Fig. 1. Principle of grid production by continuous electroforming and strip galvanizing process. The structured cylinder (shown in insert), the strip passing through the equipment, and the upper system of rolls form the cathode. The bold lines indicate the anodes.

complete industrial design of the full-scale manufacturing equipment that consists of four strip galvanizing cells. Some results reported here are based on a semi-continuous preparation mode of test grids. This consisted of the initial deposition of grid strip on a cylinder and then a plating treatment in a separate single cell. The latter was capable of coating one loop of strip that corresponded to 10 grids at a time.

The deposits were made from electrolytes of fluoborate or methane sulfonic acid. Commercially available additives were used. The alloying additions were either provided by controlled feeding of metal-rich solutions into the electrolyte, or by using pre-alloyed lead anodes.

The resulting grids were investigated by optical, scanning, and transmission electron microscopy (TEM), by micro Vickers hardness measurements and by corrosion tests in which an anodic current density of $6\,mA\,cm^{-2}$ was applied for 10 days at $75\,°C$. Weight loss, mode of attack, and grid growth were evaluated.

Fig. 2. Pilot plant for continuous electroforming and galvanizing process to produce lead grid strip.
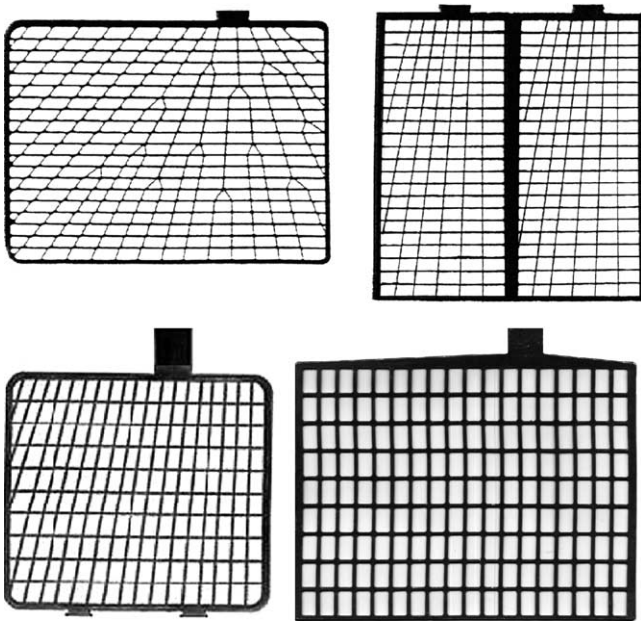
Fig. 3. Grid forms realized during development work.

3. Results

3.1. Grid geometry

Typical grid forms produced experimentally are shown in Fig. 3. The geometry of the grids produced by electroforming is determined by three features: design, average thickness, and thickness distribution.

In the electroforming process, the design may be chosen with practically no restriction. The design pattern is transferred directly as a conductive surface structure on to the deposition cylinder. In principle, any design can be realized, i.e. the design is independent of the process. The average final thickness of the grid strip is determined by the current density and deposition time throughout the electrochemical process, and can be controlled to a tolerance of about $\leq 10\,\mu$m.

The distribution of thickness depends on inherent and on predetermined factors that influence the galvanic electrode-

position process, such as edge effects, bath additives, and deliberate measures to influence the current distribution. In order to control the distribution of thickness, screens are inserted between the anodes and the strip that is being formed. As an example of deliberate thickness variation, Fig. 4 shows the distribution from the top of the lug to the lower frame of a grid. In this case, the lug was chosen to grow thicker by intent in order to provide higher strength, higher resistance to corrosion, and lower electrical resistance.

3.2. Grid composite and microstructure

The passage of the grid strip through two galvanic baths leads to the formation of a layered composite structure, as shown in Fig. 5. The core layer is deposited on the cylinder in the first cell. Its cross-section is determined by the fact that the deposition starts on the conductive pattern of the surface of the cathode. After the strip has been removed and passed through the successive galvanizing cells, the edges have become rounded.

The radial texture of the columnar crystallites, which is visible in Fig. 5, is characteristic of the galvanic deposition process. The microstructural and crystallographic features of the texture depend on the deposition parameters such as current density and bath additives [5]. Therefore, the textural features can be controlled in order to optimize the microstructure and structure of the composite.

Another microstructural feature in Fig. 5 is noteworthy, namely, the circumferential multilayer-like structure superimposed on the crystallite structure. Etching reveals that this structure results from a quasi-periodic variation of tin content and defects. These microstructural variations stem from the variations in current density and interruptions of the deposition while the grid strip enters, passes, and leaves the galvanizing cell repeatedly. This sub-structure has a favorable effect on the corrosion behavior.

The dispersion-hardened core of the grids consists of a ternary Pb–Sn–Cu alloy. Microstructural analysis by transmission electron microscopy is shown in Fig. 6 [7]. The copper-rich particles, which are dispersed within the lead
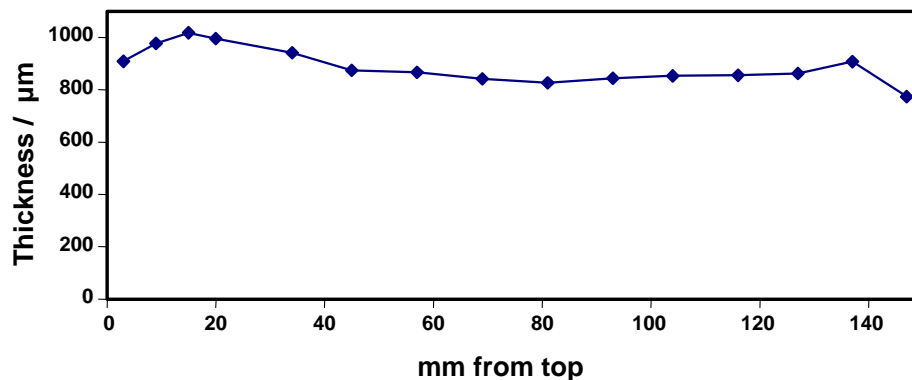

Fig. 4. Example of thickness distribution of an electroformed grid as determined by point-to-point measurements along a line from top of lug to lower frame. The lug was deliberately chosen to grow thicker.
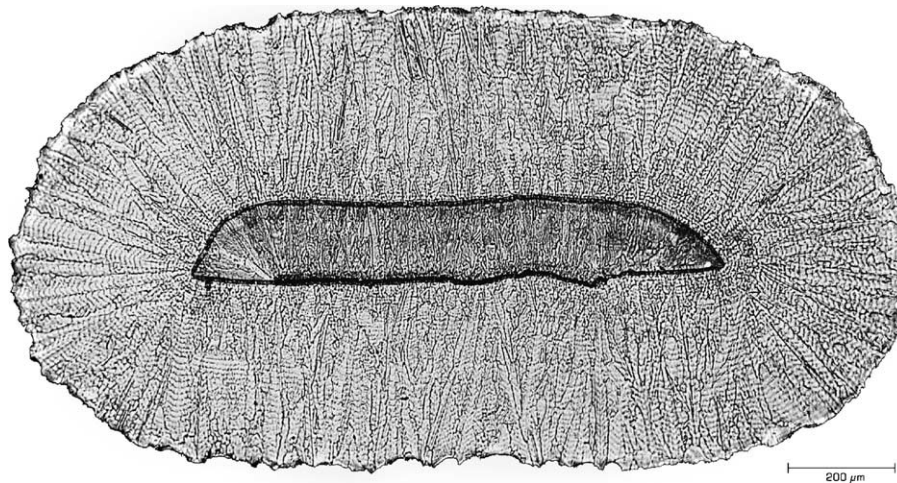
Fig. 5. Cross-sectional microstructure of grid wire. The core was formed by electrodeposition on a patterned cylinder which provides the grid structure. The outer layer was formed by subsequent strip galvanizing in a bath of different composition. Microstructural details are described in the text.

crystallites, are 5–20 nm in diameter. This size is in the optimum range for dispersion-hardening with a minimum volume fraction of particles. They are enriched in tin to such an extent that they actually constitute a tin bronze. The intrinsic hardening by tin and the surrounding strain field increase the contribution to the critical resolved shear stress and, thus, contribute to the effectiveness as particles in dispersion hardening. Some larger particles form as grain-boundary precipitates. They are less effective for hardening because of their comparatively large size and low number.

3.3. Corrosion behavior

As there is no generally accepted corrosion test for lead−acid battery grids, the grids in the present study have been subjected to a galvanostatic anodic current of 5 mA cm^{-2} at 75 °C for 10 days in accordance with the internal standard of a major international battery manufacturer. This test yields an accelerated attack which can be evaluated with respect to mass loss, grid integrity on bending, and grid growth.

Characteristic micrographs of the cross-sections of electroformed and of book-mould cast grids, before and after testing, are shown in Fig. 7. These micrographs reveal the difference in corrosion attack between the two types of grid when subjected to the same test regime. The dissolution of the electroformed grid occurs rather uniformly. A certain degree of roughness results from preferred grain boundary attack, but on a very fine scale only. The circumferential multilayer structure supports the evenness of the corrosive attack as detailed microstructural observations have shown. By contrast, the book-mould cast grid has deep crevices due to extensive grain boundary corrosion. When the corroded electroformed grid samples are bent around a cylinder of 50 mm in diameter, no wire breakage occurs. By contrast, numerous wires were broken in the book-mould cast grids.

It is well known that the rate of dissolution of battery grids in a corrosion test is difficult to define if grids of different design are compared. An exact treatment would require solving differential equations for the time dependence of the reduction in surface area for each geometrically different member of each of the grids tested. For simplification, both the current density applied and the weight loss per unit area analyzed are referred to the initial grid surface-area. This operational definition becomes more unreliable with increasing difference in grid geometry. Thus, it should be noted that the measurements given in Table 1 provide only an approximate comparison. The data indicate

Table 1

Weight loss and reduction in thickness data from a bare-grid corrosion test of experimental DSL galvanoformed grid and strip specimens and some conventional grid specimens (75 °C, 6 mA cm^{-2}, 10 days)

Specimen	Alloy content		Weight loss (mg cm^{-2})	Reduction in thickness (μm)
	Sn (wt.%)	Cu (wt.%)		
DSL grid	0.8−1.5	0	93 ± 3	83 ± 3
DSL strip	1.2–1.5	0	64 ± 13	56 ± 12
DSL strip	1.0	0.01	79 ± 7	70 ± 6
DSL strip	1.0	0.05	61 ± 6	53 ± 5
Book mould cast	Pb−0.04Ca−0.7Sn−0.03Ag−0.01Al		82 ± 4 (3)[a]	
Expanded metal	Pb−Ca−Sn		105 ± 7 (2)	
Punched grid	Pb−1Sn		65 ± 12 (2)	

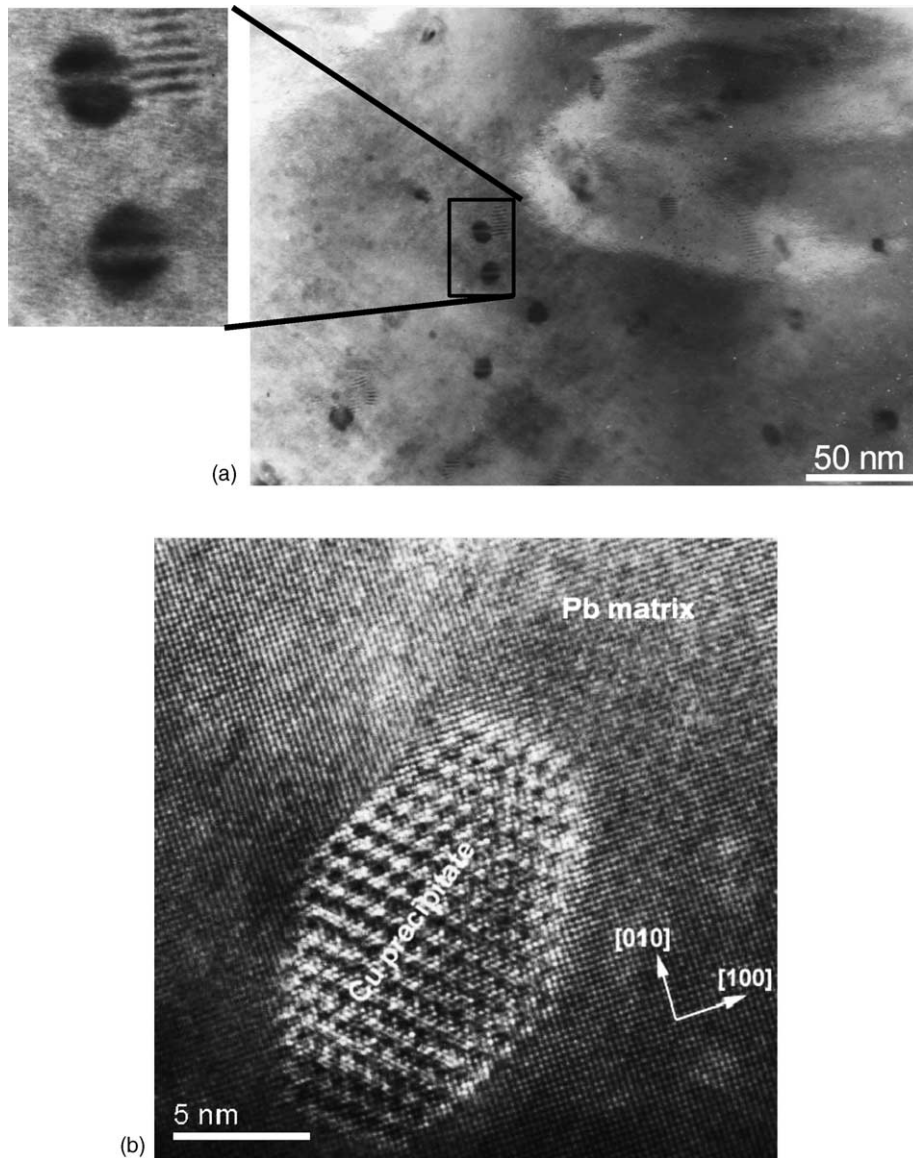[a] Number of samples tested given in parentheses.

Fig. 6. Microstructural analysis of electrodeposited, dispersion-hardened Pb−Cu−Sn alloy by transmission electron microscopy. (a) Dispersion of Cu−Sn-rich particles; enlarged area shows that the particles are associated with coherency strains; (b) high resolution image of individual particle, which indicates an epitaxial relationship to the lead matrix.

that the rate of corrosion depends on the alloy composition, but with a large scatter due to the reason given above. The mode of corrosion varies significantly with the mode of grid production. This is correlated with the fact that wires are prone to breakage upon bending after the accelerated test. The electroformed grids pass the bending test without wire breakage and this indicates that their integrity persists to a considerably lower thickness, i.e. longer life time than that of book-mould cast grids.

3.4. Grid growth

The extent of grid growth was studied along with corrosion tests of bare grids. The dimensional changes of the grid are measured along five horizontal lines and four vertical lines in 5-day intervals. Obviously, the grid growth will depend on the creep strength as an important parameter. For different layered composites, the mechanical properties of the test grids vary with the thickness ratio d(Pb–Sn–Cu layer)/d(total grid) as shown in Fig. 11 in the subsequent discussion. Accordingly, it has been found that the average grid growth during the accelerated corrosion test ($75\,°C$, $6\,mA\,cm^{-2}$) decreased from about 1% over 10 days for pure Pb–Sn material to about 0.5% over 10 days when the volume fraction of the hard Pb–Sn–Cu core in the composite grid material was increased to about 40%. Further measurements are underway.
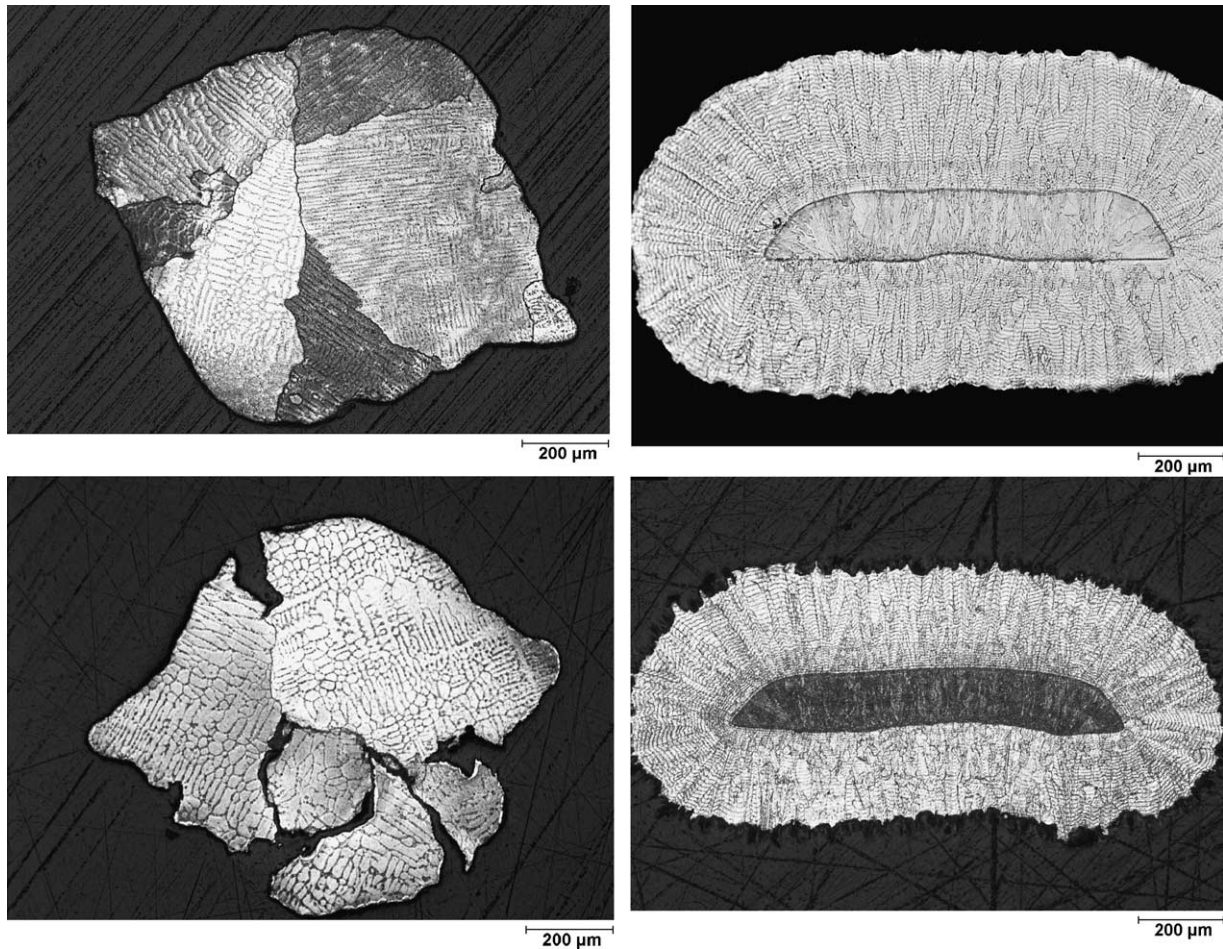
Fig. 7. Micrographs of cross-sections of grid wires before and after accelerated bare-grid corrosion test. Upper and lower left: conventional book-mould cast grid; upper and lower right: electroformed grid.

4. Discussion

The experiments have shown that efficient production of battery grids by electroforming is possible and provides a number of properties that are superior to those of grids produced by conventional processes. There follows a discussion of how these properties match the requirements for advanced lead–acid batteries.

4.1. Grid geometry

The flexibility of the electroforming process to choose the thickness and design of a grid at will is superior to that of all grid-making processes known to date. The thickness of the grid can be reduced to the minimum required by current carrying, corrosion, and handling limitations. The freedom of design allows optimization of the grid in terms of current flow or, equivalently, minimization of the resistive power loss of the plate.

The resistive power loss of plates, including the resistivity of the active mass, has been investigated by modeling and simulation of the electrical power loss of plates of different

design as a function of the design variables [6]. The starting grid design was that of a conventional cast optimized grid. The conductivity of the grid as well as that of the active mass was taken into account by using a suitable model of local current flow. A grid weight of 30 g, a minimum grid thickness of 0.4 mm and a minimum wire width of 0.7 mm were assumed to satisfy the requirement of mechanical stability. The simulation was carried out for a number of different positions of the lug and a minimum number of horizontal grid wires required for mechanical stability. A typical result is shown in Fig. 8. The grid structure is simplified and the total electrical loss is reduced by 22%. This may be taken as a characteristic order of magnitude for the possible reduction of electrical loss per plate by the freedom of design provided by using electroformed grids.

4.2. Composite structure

By its very nature, the continuous electroforming process has the capability to produce a layered composite material because the successive galvanic cells can be operated with different electrolytes and under different deposition

Present design
Power loss: 5.91

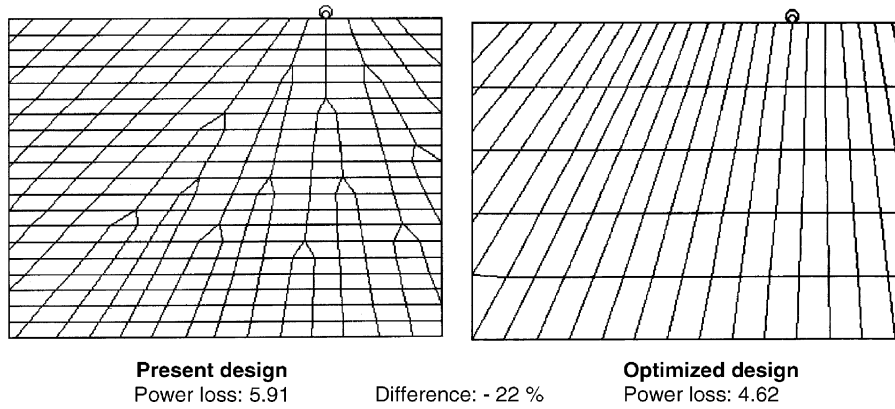Difference: - 22 %

Optimized design
Power loss: 4.62

Fig. 8. Modeling of power loss minimization of an automotive battery plate. Plate size: 143 mm × 10.6 mm × 0.4 mm. Grid weight: 30 g. Minimum wire width: 0.7 mm.

conditions. By way of example Fig. 9 shows a schematic drawing of how this capability can be utilized to produce a composite grid with optimized functional layers. The example given is self-explanatory. It should be noted, however, that a wide range of variability of the composition, microstructure, and thickness of the individual layers can be provided by this feature of the technology. A predetermined thickness ratio of hard and soft layers can serve to tailor the macroscopic mechanical properties of a grid to a given specification, as discussed below.

4.3. Mechanical properties

The electrochemical process enables the production of a dispersion hardened Pb–Sn–Cu alloy, as illustrated microscopically in Fig. 6. In order to prevent copper from poisoning the electrolyte, the bronze-hardened alloy is used in the core layer of the grid only. Due to the extremely low solubility of copper in lead, a significant amount of dispersed bronze particles occurs upon electrodeposition. The resulting yield stress varies with the copper and tin contents, as shown in Fig. 10. Pure-copper particles provide a moderate increase in hardness. The bronze particles cause a much greater increase. On this basis, the core layer of the grids can be hardened to a required level. The macroscopic yield

stress of the grid is then given by the yield stress of the composite. The latter is obtained, to a good approximation, by adding the fractional yield stress contributions of the layers, as shown in Fig. 11. Thus, the yield stress values of conventional Pb–Ca–Sn–(Ag, Al) or any other value in the accessible range can be matched.

4.4. Growth minimization

The amount of grid growth caused by oxidation is obviously a major concern with new grid materials. The extent of growth depends on the creep strength of the material, the cross-section of the grid wires, and the geometry of the grid design. The growth behavior has been simulated as a function of the stress−strain behavior of the material (for lack of creep data) and of the wire cross-section. The stress due to oxidation was simulated by a volume stress occurring inside the grid cells. Although this is not exactly the stress distribution which actually occurs, it is still a good approximation such that it can be surmised that the computed stresses and strains of the present, approximate model are scaling with those of a refined, more exact model. A pictorial representation of the local detail of grid growth geometry according to the present model is given in Fig. 12, and quantitative results obtained from calculations for complete grids are presented

Core layer: grid stucture, arbitrary design

1st coating layer: providing corrosion resistance

Controlled roughening: supporting paste adherence

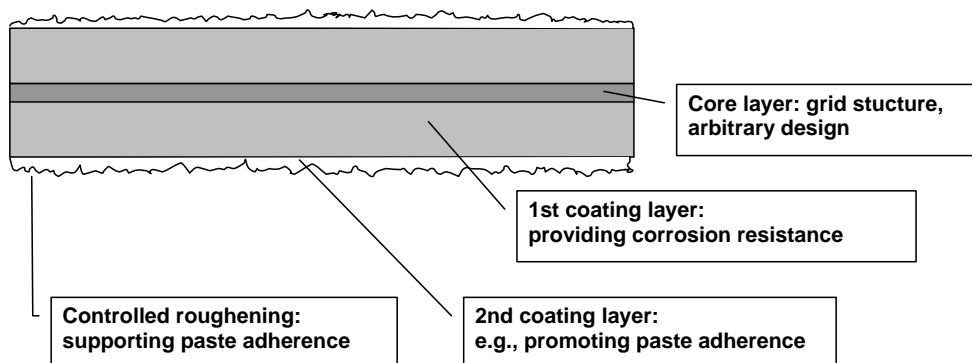**2nd coating layer: e.g., promoting paste adherence**

Fig. 9. Schematic representation of layered composite structure of a battery grid that can be produced by electroforming in a succession of galvanic cells.
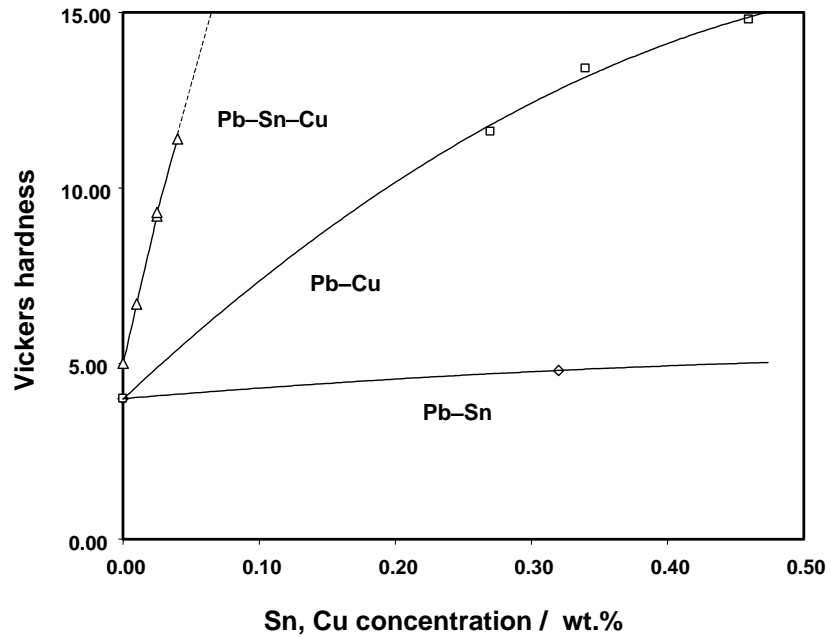
Fig. 10. Variation of Vickers hardness of electroformed Pb−Sn, Pb−Cu, and Pb−Sn−Cu alloys.

in Fig. 13. The indices u_x and u_y refer to the maximum horizontal and vertical displacements, respectively. The curves marked Pb refer to pure lead with a yield stress $R_{p0.2} = 7$, while the curves marked Pb–X refer to an alloy or composite with $R_{p0.2} = 28$. It should be noted that the curves are referring to two scales, indicated left and right on the ordinate, which differ by a factor of 10. The displacements computed differ by a factor of about 5 between the soft and the hard material. Similarly, for one material the variation in width (i.e. cross-section) in the range 400–900 μm also leads to a variation in growth displacement by a factor of

about 5. Such dependencies are a very helpful guide to specify the grid strength and wire cross-section. In addition, the freedom of grid design given by electroforming offers a further opportunity for growth minimization. This is presently under examination and is producing promising preliminary results.

4.5. Adherence of the positive active material

As indicated in the schematic drawing of a possible layered composite structure (Fig. 9), the continuous
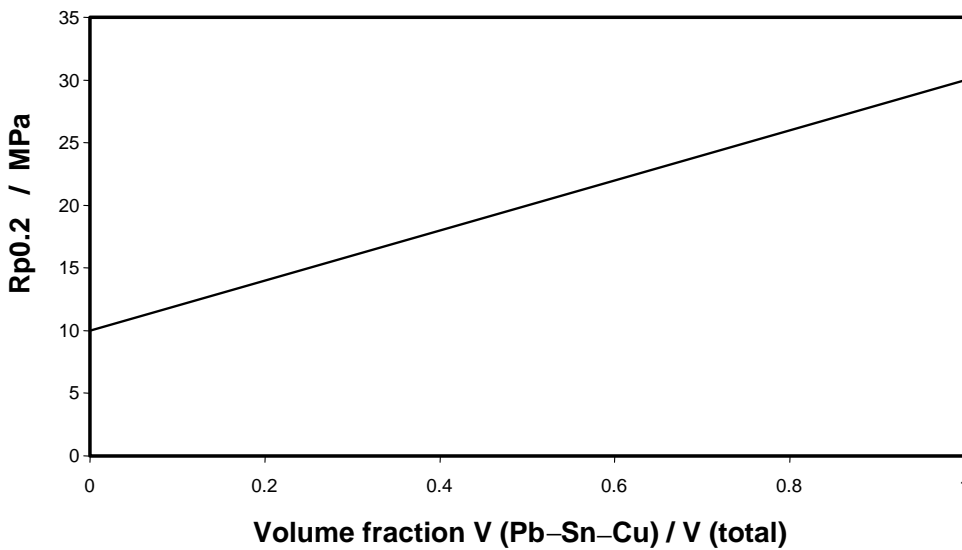

Fig. 11. Variation of approximate macroscopic yield stress of a composite of Pb−Sn−Cu and Pb−Sn layers as a function of the volume fraction V(Pb−Sn−Cu)/V(total) of the hardened core layer of an electroformed composite grid.
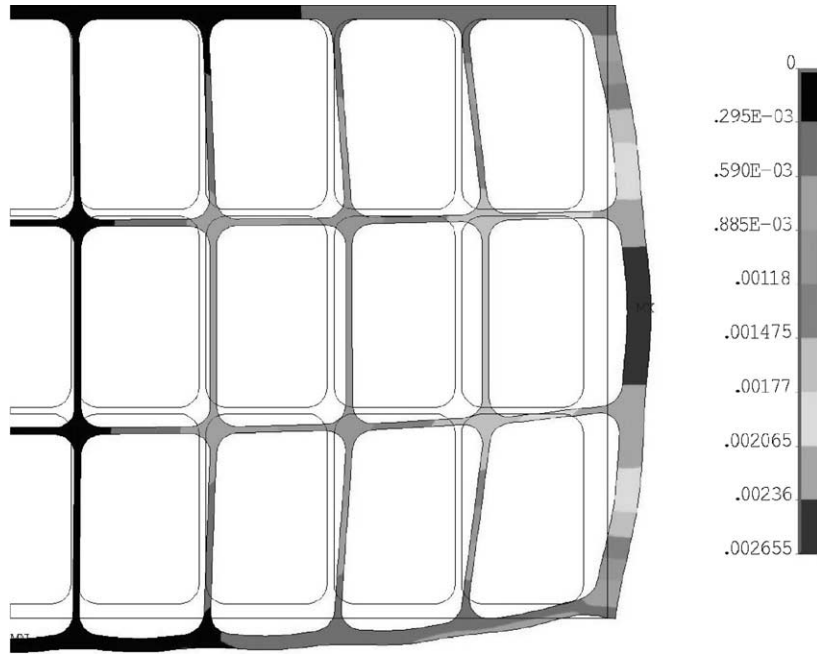
Fig. 12. Simulation of grid growth: pictorial view of a displacement pattern.

electroforming process provides the technical conditions to produce a surface layer that combines two properties to improve the adherence of the positive active material. These two conditions and properties are: deposition of an alloy layer to increase the chemical bond, and imposing a predetermined roughness of the final surface to increase the mechanical bond to the active material. A Pb−Sb alloy may be suitable for deposition to increase chemical bond-
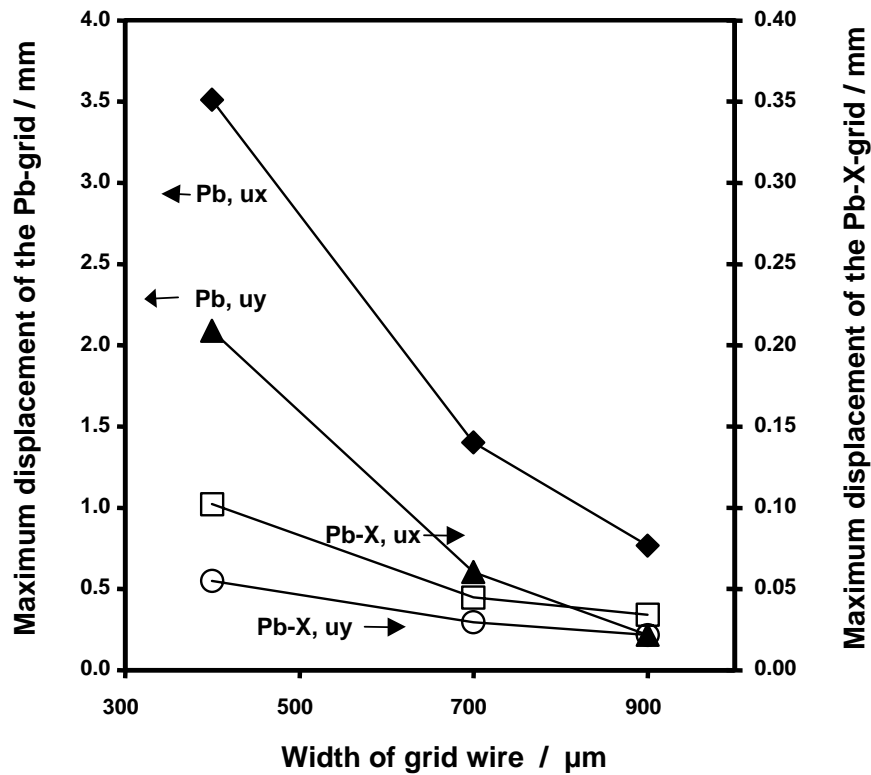
Fig. 13. Simulation of grid growth: dependence of maximum displacements u_x (width) and u_y (height) as a function of material properties (pure Pb vs. hardened Pb–X alloy) and varying grid thickness ($400 = d = 900 \,\mu$m).

ing. This would be analogous to the surface coating by roll plating of a Pb−Sb alloy [8]. At variance, to the plating of strip before the slitting and expanding process, which leaves the cut faces uncoated, the electrodeposition process will coat the grid completely, and thus, will provide better bonding all around. Additionally, the roughness of the grid surface can be varied by controlling the deposition conditions within a wide margin. Experimental roughness traces of electrodeposited lead surfaces are shown in Fig. 14. The current density was controlled and varied deliberately to ob-

tain a range of variation that would improve the mechanical adherence of the active material.

4.6. Economic considerations

Since no innovative technological development is viable without economic competitive advantages, all cost factors have been minimized from the start. It is considered that the process manufactures grids at a cost no higher than that of competing processes such as the expanded-metal and the
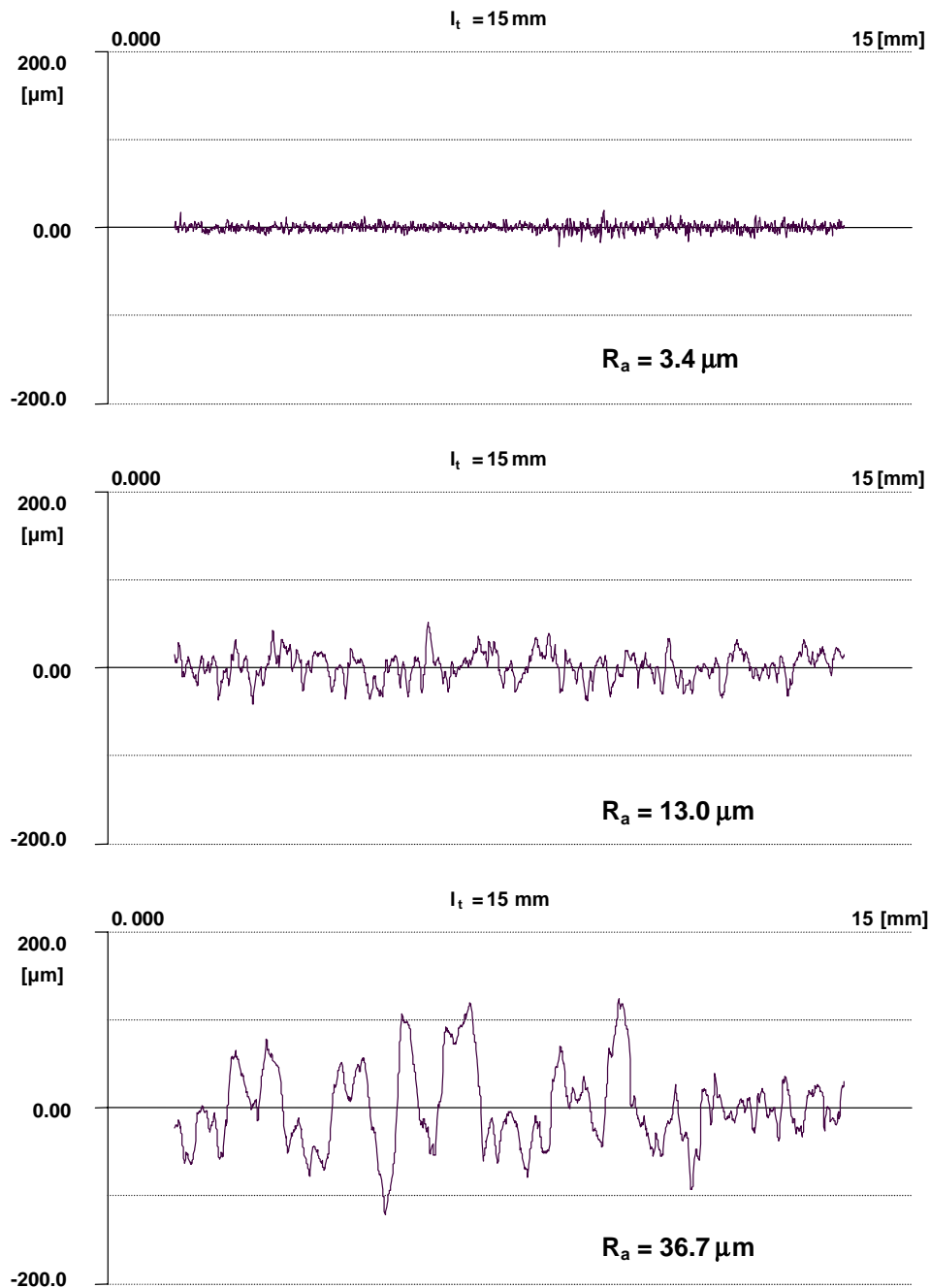

Fig. 14. Roughness traces of experimental galvanic Pb deposits that show the range in which controlled roughness can be applied to the surface of electroformed grids.

stamped-grid technologies. The process is economical for production units that yield about 100 grids per minute according to a specific design of a commercial production unit.

The possibility of significant cost reduction is provided by the freedom of design, i.e. reduction in thickness and optimized grid structure. It is estimated that these two contributions to weight saving may add up to a 20–30% reduction in raw material costs. A further advantage is the use of battery scrap instead of virgin material in the process. This is related to the fact that electrolysis is inherently accompanied by a refining process. According to expert estimates, the use of scrap instead of virgin material can amount to savings of up to 20–30% in the cost of raw materials.

As the reduction in lead mass per grid is also leading to a reduction in battery weight, this may by an added value to the customer and is assessed by the car industry to be of the order of US$ 5 per kg.

5. Conclusions

Grid production by continuous electroforming has been shown to be technically advantageous and economically attractive. The freedom in grid thickness and grid design is providing lower weight, lower losses, and lower costs. The inherent formation of a fine-grained columnar microstructure and a layered composite is providing flexibility in optimizing surface properties for increased corrosion resistance and adherence of the positive active material. The possible use of battery scrap as raw material directly in the process provides an additional decrease in costs.

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