

A method for producing electrolytically coated cold band, preferably used for the manufacturing of battery shells, and for battery shells manufactured according to this method

This invention relates first to a method for producing electrolytically coated cold band, preferably used for the manufacturing of battery shells, during which the cold band is electrolytically coated with a layer of cobalt or cobalt alloy.

In general, battery shells are manufactured of a cold band electrolytically coated with multiple layers. Document EP 0 629 009 B1 describes a cold band as well as a method for producing cold band electrolytically plated with nickel that is characterized by a favorable behavior during a subsequent drawing and ironing process. In order to improve the effective contact surface between the inner side of the battery shell and the cathode material, a hard coating of a nickel layer is deposited on the side of the cold band that will later form the inner side of the battery shell. During the drawing and ironing process, cracks form in this layer resulting in an enlargement of the contact surface.

A similar material is described in document EP 0 809 307 A2. The side of the band material that will later form the inner side of the battery shell is coated with a hard material layer, whereas the other side – which will later form the outer side of the battery shell – is coated with a relatively soft metal layer. To achieve a hard metal coating, this document proposes electroplating process with an alloy on the nickel basis. Document EP 0 809 307 A2 indicates various examples of the hardness of thus produced alloys. It also mentions the possibility to add organic ingredients to the galvanic bath; however, no indication regarding the hardness properties of layers produced with these baths is made. During the subsequent forming of the metal sheet into battery shells, brittle fractures are supposed to form in the electrolytically deposited hard alloy coating which results in an enlarged surface and, therefore, reduced electrical contact resistance between the cathode substance of the battery and the inner surface of the battery shell.

In general, the use of organic ingredients in galvanic bath has been known for a long time as documented, e.g., by US patent 2,026,718 from 1936. This document describes the addition of aromatic sulfonic acids to the galvanic bath for the purpose of achieving a glossy layer.

The use of organic ingredients in galvanic nickel, cobalt, and nickel-cobalt baths for producing an improved cold band for the manufacturing of battery shells has also been known. So, e.g., document patent DE 19 53 707 A1 describes a procedure, during which layers of nickel, cobalt or of their alloys are deposited after an unsaturated, organic substance such as butyne diol has been added to the electrolyte. This document proposes deposition with inert anodes in a halogen-free bath at a current density of  $83.8 \text{ A/dm}^2$ , where the process is controlled in such a manner as to avoid brittle deposits.

Finally, it is known from the state of art how to deposit cobalt from a galvanic bath with the aid of organic substances in order to form, e.g., ferromagnetic layers for data carriers (see, e.g., patent US 4,756,816).



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The underlying task of this invention is to develop a procedure for electrolytical production of cold band that would allow – during the manufacturing of battery shells by drawing and ironing – to achieve low values of the electrical contact resistance between the cathode substance of the battery and the inner side of the cupular battery shell. Furthermore, the invention is to propose the manufacturing of a battery shell according to such procedure and by subsequent forming operation.

To resolve this task, the invention proposes, for the procedure of the initially mentioned nature, that organic substances that create decomposition products be added to the electrolyte during the coating process and that these decomposition products and/or reaction products of these decomposition products with other ingredients in the galvanic bath are deposited on the band material together with cobalt or the cobalt alloy.

Thus produced cold band is characterized in that its side coated with an electrolytical layer, if subjected to strong forming forces as they occur during drawing and ironing of the material to produce, e.g., a battery shell, shows an especially low electrical contact resistance. The cause of this phenomenon is that the brittle layer of cobalt or a cobalt alloy cracks and forms individual plates separated by fissures. Due to these fissures, the electrical contact resistance is diminished, which is why the band produced in a procedure according to this invention is especially suitable as the basis material for the manufacturing of cupular battery shells by deep-drawing or drawing and ironing, and especially for batteries with alkaline electrolytes. Compared to the current state of art, the inner side of the thus manufactured battery shell demonstrates even lower values of the electrical contact resistance between the cathode substance of the battery and the inner side of the battery shell.

In order to achieve the desired brittleness and to improve the electrical conductivity of the electrolytically produced layer, the process conditions should preferably be selected in such a manner that the resulting coating contain a cobalt share of more than 35 weight percent. Furthermore, it is advantageous if the current density of the electrolyte bath lies within a relatively narrow range of no more than  $10 \text{ A/dm}^2$ , preferably in a range between 6 and  $8 \text{ A/dm}^2$ .

Also important for the subsequent forming process of the produced galvanic coating is the chloride content in the electrolyte bath. This should be more than 24 g/l, preferably more than 30 g/l.

Another preferred version of the procedure proposes that the cobalt alloy contain the ingredients of nickel, iron, tin, indium, palladium, gold and/or bismuth that reduce the contact resistance of the subsequent battery shell manufactured by a forming process. These ingredients can be used as a simple admixture or in coatings made of more than two of these elements.

A raw material especially suited for the production of the cold band is steel with a carbon content of less than 0.20% of a thickness of 1 mm and preferably of 0.1 – 0.7 mm. According to a first version, the brittle coating can be deposited directly on the base material made of steel.

According to a second version, the brittle coating is deposited on a layer arranged underneath and deposited previously in a galvanic process. This layer arranged underneath is preferably an electrolytically deposited, and subsequently homogenized nickel layer that demonstrates an

excellent corrosion resistance. Afterwards, the material is coated with a layer of a high cobalt content with embedded decomposition products of organic ingredients. Although during the subsequent strong forming process by deep-drawing or drawing and ironing the cobalt layer cracks, such cracks do not reach all the way down to the steel base material but, rather, they are stopped by the underlying ductile nickel layer so that the corrosion resistance remains intact.

In another version, the layer according to this invention with a high cobalt content is coated with an additional layer that leads to a better surface conductivity of the battery shell manufactured from the band material by deep drawing. Suitable for such coating is, e.g., gold or palladium. In this version of the cold band too, the hard, brittle cobalt layer including the additional coating of gold or palladium (that it carries) cracks during a subsequent deep drawing or drawing and ironing. In this manner, the advantage of a brittle layer with regard to the electrical contact resistance of the band material can be combined with the advantage of a particularly good conductivity of the surface.

Furthermore, it is possible - before the deposition of the brittle layer with a high cobalt content - to coat the material with a layer with embedded, electrically conductive particles such as carbon particles. In this case, the subsequent cracking of the coating creates fissures that reach down to the electrically conductive particles in the material, by which process the particles are now partially located on the surface of the band material. In this variant, the positive properties of a coating with imbedded particles such as carbon particles with regard to conductivity are combined with the previously described positive properties of the coating with a high cobalt content that will be later cracked.

Another preferred variant of the procedure according to this invention proposes that the layer of cobalt or a cobalt alloy be applied onto both sides of the cold band, that both coatings occur in the same electrolyte bath but with different current densities so that the current density during the coating of the side that will later form the outer side of the battery shell is set up differently from the current density during the coating of the side that will later form the inner side of the battery shell. The additional layer on the subsequent outer side of the battery shell brings substantial advantages during the deep drawing or drawing and ironing of the battery shell because the danger for the particles to deposit on the deep-drawing tool is reduced. In this way, during a single treatment step the good drawing properties of a metal sheet with a cobalt coating are combined with good properties with regard to the performance of the final battery achieved due to the brittle coating on the inner side.

This result can also be achieved by first applying such a coating to at least the side of the cold band that will later form the outer side of the battery shell, that contains nickel grains of a smaller size due to, e.g., the addition of grain refining agents, and then homogenizing the material. A suitable grain-refining agent is, e.g., para toluol sulphonamide. In a second procedure step, i.e., after the homogenizing or possibly rerolling or killing, the above described brittle layer of cobalt or a cobalt alloy is applied on the side of the cold band that will later form the inner side of the battery shell. The thus produced material combines the material properties of the outer side advantageous for deep-drawing and drawing and ironing process with the required excellent contact capability on the inner side of the subsequently formed battery shell.

During the procedure according to this invention the organic ingredients in the electrolyte disintegrate into decomposition products due to the stream flowing in the electrolyte during the galvanization process. These decomposition products can react with other components of the galvanic bath, especially with metal ions. The thus obtained reaction products are deposited on the cold band together with other decomposition products and with the cobalt or cobalt alloy, and cause an imbrittlement of the coating. In case of organic substances containing sulfur or carbon, these reaction products might be, e.g., cobalt sulfides or cobalt carbides.

Among organic ingredients suitable for addition to the cobalt-containing electrolyte are brighteners known from the galvanic nickel-plating process. Also suitable are preferably brighteners called secondary brighteners. A typical example of this group is butyne diol. Galvanic deposits with these ingredients in the cobalt electrolyte bath result in a very hard and, at the same time, brittle coating, which is why the material tends to form strong cracks during the subsequent forming processes. The arising fissures are characterized by a relatively homogeneous structure with a lozenge shape of the individual fissure plates.

During the tests, after the cold band produced according to this invention has been subjected to a deep-drawing process, the average length of the plate edge turned out to be between 3 and 50  $\mu\text{m}$ . The form and the edge length of the produced lozenge-shaped fissure plate is of decisive importance for the performance of the batteries subsequently manufactured from the band material.

In this connection, it is of a special advantage that, during the forming process to manufacture a battery shell, the brittle coating of the cold band produced by a procedure according to this invention always cracks in such a manner that the fissures run not in the longitudinal direction of the battery shell but rather at an angle of about  $45^\circ$  to this direction. This is of a particular importance, because during the manufacture of the batteries a cathode mass is pressed into the battery shell, which has been previously pressed into the so-called "pellets". These pellets are rings or disks made of a mixture of manganese dioxide, carbon, caustic potash solution and a binding agent. A functional contact for the conducting of electrons is endeavored during the pressing of the rings into the battery shell. Since during the forming process the band material produced by a procedure according to this invention forms fissures at an angle of  $45^\circ$  to the forming direction, during the pressing of the pellets into the battery shell a portion of the cathode mass can enter the fissures running at an angle to the pressing direction. This circumstance results in an especially good contact between the cathode mass and the inner side of the battery shell. This advantage of an improved contact is combined with the advantage of a good storage life of a battery shell coated with cobalt on its inner side. As a result, this allows manufacturing batteries that are characterized not only by an excellent contact of the cathode mass with the inner side of the battery shell due to the cracked surface, but also by an excellent storage life due to the cobalt coating. This applies accordingly also to a graphite layer arranged on this coating before the filling of the battery shell with the cathode mass, where, however, it is not the direct contact of the cathode mass with the battery shell but rather the contact of the graphite layer with the battery shell due to a strong anchoring of the graphite on the inner side of the battery shell.

Figure 3 shows a table of examples of coated cold bands produced with the parameters of this invention. The organic ingredients to the electrolyte bath in Figure 3 designated with V1 to V4 are as follows:

- V1: butyne diol
- V2: A mixture of butyne diol and saccharine. In the table of Figure 3, in the cell "concentration" the first number relates to the concentration of butyne diol, and the second number relates to the concentration of saccharine.
- V3: Para toluol sulfonamide
- V4: Saccharin

In addition, Figure 3 shows, among other things, the pH value, temperature, chloride content, the concentration and the current density of each particular electrolyte bath used. And finally, the table indicates each particular behavior of the coated cold band during the subsequent forming process of deep drawing or drawing and ironing as well as the average edge length of the lozenge-shaped fissure plates arising during the deep-drawing process. These edge lengths are, e.g., also illustrated in Figure 2.

Figure 1 shows an enlarged fissure pattern of example 27 marked with an "\*" in Figure 3, Figure 2 shows example 9 marked with "\*\*\*".

Patent Claims

1. A procedure for producing an electrolytically coated cold band, preferably used for the manufacturing of battery shells, during which the cold band is coated with a layer of cobalt or a cobalt alloy in a galvanic process, characterized in that during the coating process, organic substances are added to the electrolyte that create decomposition products, and that these decomposition products and/or reaction products of these decomposition products with other components of the galvanic bath together with the cobalt or a cobalt alloy are deposited on the band material as a brittle layer.
2. A procedure according to claim 1, characterized in that the cobalt content in the electrolytical coating is higher than 35 weight percent.
3. A procedure according to claim 2, characterized in that the cobalt alloy used to improve the electrical conductivity of the battery shells formed from the cold band by a deep-drawing process, contains an admixture of nickel, iron, tin, indium, palladium, gold and/or bismuth.
4. A procedure according to one of the preceding claims, characterized in that a steel type of a carbon content of less than 0.2% and of a thickness of up to 1 mm is used as the base material.
5. A procedure according to one of claims 1 to 4, characterized in that the brittle coating is deposited directly on the metal base material, especially steel.
6. A procedure according to one of claims 1 to 4, characterized in that the brittle coating is deposited on a layer arranged underneath it that has been deposited in a preceding procedure step.
7. A procedure according to claim 6, characterized in that the layer arranged underneath is an electrolytically deposited nickel layer that was subsequently homogenized.
8. A procedure according to claim 7, characterized in that during the electrolytical depositing of the layer arranged underneath a grain refining agent such as para toluol sulfonamide is added to the galvanic bath.
9. A procedure according to one of claims 1 to 4 and/or 6 to 8, characterized in that the brittle coating is deposited on a layer arranged underneath that contains embedded electrically conductive particles.
10. A procedure according to claim 9, characterized in that the electrically conductive particles are carbon particles.

11. A procedure according to one of the preceding claims, characterized in that the organic electrolyte ingredients, whose decomposition products and/or reaction products arising from reactions of these decomposition products with other components of the bath are integrated into the coating, are brighteners (the so-called secondary brighteners).
12. A procedure according to claim 11, characterized in that the brighteners are butyne diol with/without the addition of o-benzosulfimide (saccharine).
13. A procedure according to one of the preceding claims, characterized in that the current density of the electrolyte bath is under  $10 \text{ A/dm}^2$ , preferably 6 to  $8 \text{ A/dm}^2$ .
14. A procedure according to one of the preceding claims, characterized in that the chloride content in the electrolyte bath is higher than 30 g/l.
15. A procedure according to one of the preceding claims, characterized in that the coating made of cobalt or a cobalt alloy is applied onto both sides of the cold band, that both coatings occur in the same electrolyte bath but at different current densities, where the current density during the coating of the side that will later form the outer side of the battery shell is set up differently from the current density during the coating of the side that will later form the inner side of the battery shell.
16. A battery shell, characterized in that it is manufactured by a forming process, especially by deep drawing or drawing and ironing from a cold band produced according to one of claims 1 to 15.