File Number: T 556/91 - 3.4.2
Application No.: 86 114 677.7
Publication No.: 0 267 972
Title of invention: A method for the electrodeposition of an ordered alloy


DECISION
of 25 February 1992

Applicant: Technion Research & Development Foundation Ltd.

Headword: EPC Article 56
Keyword: "Inventive step - yes, after amendment"

Headnote
Case Number : T 556/91 - 3.4.2

DECISION
of the Technical Board of Appeal 3.4.2
of 25 February 1992

Appellant :
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Decision under appeal :
Decision of Examining Division of the European
Patent Office dated 15 February 1991 refusing
European patent application No. 86 114 677.7
pursuant to Article 97(1) EPC.

Composition of the Board :
Chairman : E. Turrini
Members : M. Chomentowski
          C.V. Payraudeau
Summary of Facts and Submissions

I. European patent application No. 86 114 677.7 (Publication No. 0 267 972) was refused by the Examining division on the grounds that the subject-matter of Claim 1 lacked an inventive step with regard to

D1: Plating & Surface Finishing, vol. 73, no 5, May 1986, pages 130 to 134, C. OGDEN: "High-strength, composite copper-nickel electrodeposits".

During examination proceedings,

D2: Journal of the Electrochemical Society, 130, October 1983, No. 10; pages 1987 to 1994; U. COHEN et al, "Electroplating of cyclic multilayered alloy (CMA) coatings"

was also mentioned.

II. The Appellant (Applicant) filed an appeal against this decision. He requested that the decision under appeal be set aside and that a patent be granted on the basis of new claims.

III. The presently valid Claim 1 reads as follows:

"1. A method for the electrodeposition of a composite foil consisting of substantially pure layers of one metal alternating with substantially pure layers of another metal each layer having a thickness of less than 9 nm,

(A) by electrolysing a bath

(a) comprising a solution of two metals chosen such that the redox potential gap between the more
noble metal and the less noble metal is at least 0.1 V,

(b) wherein the concentration of the more noble metal ion is in the range of 0.001 to 1.0 M and

(c) the concentration of the less noble metal ion is near the level of saturation thereof at room temperature;

(B) applying a frequency between 0.02 Hz and 15 Hz and a potential to the cathode at a first value which is selected so as to be between the potentials at which the metals begin to deposit under the conditions used, for a sufficient time to deposit less than 9 nm - preferably 0.2 to 5 nm - thickness of substantially pure more noble metal;

(C) changing the potential applied to the cathode to a second value which is selected so as to be substantially more negative than the potential at which the less noble metal begins to deposit under the conditions used, the potential being increased until the total current density is higher than the limiting current density for the more noble metal so that the percentage of more noble metal in the less noble metal layer approaches zero, thereby permitting deposition of substantially pure less noble metal, the potential being applied for a sufficient time to deposit less than 9 nm - preferably 0.2 to 5 nm - thickness of the substantially pure less noble metal; and
(D) repeating step (B) and (C) for a predetermined number of cycles to obtain a corresponding number of layers of the metals."

Claims 2 to 7 are dependent claims.

IV. The Appellant submitted the following arguments in support of his request. The invention relates to a method for the electrodeposition of a composite foil consisting of alternated substantially pure layers, which are achieved by selecting, in a single electrodeposition bath, the concentration of the more noble metal (Copper) to be very low and that of the less noble metal (Ni) to be near the level of saturation at room temperature; because of the purity of the component layers and of their small thickness (less than 9 μm), the formed composite layer has in particular a high modulus of elasticity; a comparative experiment, carried out under the same conditions as in example 1 of the specification, except that the concentration of NiSO₄.6H₂O is 60 g/l instead of 330 g/l, results in layers of nickel containing about 10% copper, with the effect that the modulus of elasticity is only 20% greater than that of the homogeneous alloy with the same average composition, and not 250%, as the resulting layer of the example 1. It is possible to avoid deposition of the more noble metal if only deposition of the less noble metal is desired because deposition of the more noble metal is restrained by a diffusion barrier due to the difference in concentrations in the solution (0.005 M to 1 M for the noblest metal, as compared to a concentration of the less noble metal being as high as possible). Other important features of the invention are the frequency applied, which is between 0.02 and 15 Hz, and the potential applied to the cathode, which is at a first value between the potentials at which the metals begin to deposit under the conditions used. The only relevant prior
art is D1, which only partially deals with single electrolytic baths, all experimental data given before page 133, left-hand column, second section being concerned with preparing composite copper nickel foils by plating alternately from copper sulfate and nickel sulfamate baths. D1 discloses, in relation with the part dealing with electrodeposition from a single electrolytic bath, that quality nickel deposits could not be obtained at all deposition potentials apparently due to excessive co-deposition of copper. Thus, although D1 intends to achieve foils consisting of substantially pure layers, the deposition of the more noble metal is not restrained by a diffusion barrier during deposition of the less noble metal because, contrarily to the present invention, D1 does not suggest to select the concentration of the less noble metal in the electrodeposition bath to be near the level of saturation at room temperature. Therefore, the method of Claim 1 implies an inventive step.

V. In a communication dated 15 January 1992, the Board expressed the provisional opinion that the subject-matter of Claim 1 implied an inventive step and that a patent could be granted on the basis of the submitted claims together with a correspondingly amended description. A copy of the specification incorporating the amendments considered as necessary by the Board was annexed to the communication.

VI. In a written statement filed in answer to the communication, the Appellant requested the grant of a patent on the basis of the specification amended as proposed by the Board.
Reasons for the Decision

1. The appeal is admissible.

2. Allowability of the amendments

2.1 Claim 1 results from the combination of Claim 1 and Claim 2 (for the feature that the concentration of the less noble metal ion is near the level of saturation thereof at room temperature), both as originally filed, and with the additional feature, disclosed on page 4, lines 2 to 10, as originally filed, that the applied frequency is between 0.02 Hz and 15 Hz. Therefore, the Board is satisfied that the European patent application has not been amended in such a way that it contains subject-matter which extends beyond the content of the application as filed (Article 123(2) EPC).

3. Clarity of the claims

3.1 Claim 1 mentions that the deposited composite foil consists of substantially pure layers of a more noble metal and of a less noble metal, whereby in particular the percentage of the more noble metal in the less noble metal layer is specified as approaching zero. In relation with these features, it is to be noted that the valid patent application (see page 5, last section to page 6, first complete section) mentions that the controlled level of presence of more noble metal in the layers of less noble metal is according to the equation

\[ P_m = \frac{IL}{IT \cdot n} \]

whereby

IL = the limiting current depository for the noblest metal electrodeposition depending on metal concentration and agitation, 

n = the cathodic efficiency,
IT = the total current density applied during the electrodeposition of the less noble metal layer, and that, when IL / IT is much less than 1, the Pm tends towards zero, which means that the less noble metal layer can be formed practically pure.

Moreover, Claim 1 mentions that, in the electrolyzing bath, the concentration of the less noble metal ion is near the level of saturation thereof at room temperature. In relation with this feature, it is to be noted that the valid patent application (see page 7, last section; see also page 4, last section, lines 7 to 15 and page 5, second section, last sentence) specifies that one of the critical parameters found to be required for the claimed method is the concentration of the noblest metal in the solution to be in the range of 0.001 M to 1 M, at which concentration the limiting current density is low enough to ensure dilution of this metal in the layers of the other metal so that the latter can be produced practically pure, and that the concentration of the less noble metal is set as high as possible (near the saturation) considering solubility data and maintaining the minimum redox potential gap.

3.2 Therefore, the Board is satisfied that the features of the claimed method are unambiguously defined and that, accordingly, the claim is clear in the sense of Article 84 EPC.

4. Novelty

4.1 A method for the electrodeposition of a composite foil consisting of layers of one metal alternating with layers of another metal is known from D1 (see page 130, the abstract, first sentence; page 134, the summary, first
sentence). However, in particular, contrarily to the method presently claimed, the deposited layers of D1 (see page 130, right-hand column, second section, last sentence) have not a thickness of less than 9 nm, but are mentioned as being "macromodulated" with a thickness of the layers that varies from 0.4 to 8.2 μm.

4.2 Another method for the electrodeposition of a composite foil consisting of layers of one metal alternating with layers of another metal is known from D2 (see the abstract); in particular, a structure composed of relatively thin layers of a first metal alternating with layers of a second metal can be produced by cyclic modulation of the cathode current during electrodeposition. However, in particular, contrarily to the method of Claim 1, D2 (see especially page 1988, left-hand column, third section, first sentence and last section, first sentence), does not mention the deposition of pure metal layers and stresses the small magnitude of the obtained composition modulation (usually no more than about 20-30%) of the alternating Pd-rich and Ag-rich deposited alloys.

4.3 The other documents of the available prior art only disclose isolated features of present Claim 1 and are thus less relevant.

4.4 Therefore, the Board is of the opinion that the subject-matter of Claim 1 is novel in the sense of Article 54 EPC.

5. Inventive step

5.1 The Board is of the opinion that, as mentioned by the appellant, only a part of D1 deals with depositing copper nickel-foils from a single electrolyte bath; indeed,
multilayer deposition using two baths is stressed in D1 (see in particular page 130, right-hand column, second line to page 131, left-hand column, first line; see also page page 131, left-hand column, last section, two first sentences).

5.2 D1 (see page 130, the abstract, second sentence; page 134, the summary, second sentence) also teaches that electrochemical experiments show that it is feasible to develop a single electrolyte for depositing copper-nickel multilayer coatings by synchronously modulating the electrode potential and the rate of solution mass transport. Thus, it is derivable from D1 (see page 130, the abstract; left-hand column, first section, last sentence and right-hand column, second section, last sentence; page 131, left-hand column, first section, last sentence to third section; page 132, left-hand column, second and third section; page 133, left-hand column, second section to page 134; Figures 4 to 5) that, in said suggested method, wherein the layer of the more noble metal (Cu) can be deposited as a pure metal (100%), the layers can be deposited

(A) by electrolysing a bath

(a) comprising a solution of two metals chosen such that the redox potential gap between the more noble metal and the less noble metal is at least 0.1 V,

(b) wherein the concentration of the more noble metal ion is specified as being low, from 0.00 to 0.01 M CuSO₄, in particular 0.005 M and 0.010 M, and thus in the range of 0.001 to 1.0 M, and
(c) the concentration of the less noble metal ion is specified as being higher, and in particular 1.25 M NiSO₄ (and thus higher than the concentration of the more noble metal ion from 0.00 to 0.01 M CuSO₄); B, C & D) by modulating the electrode potential, i.e.

(B) applying a frequency and a potential to the cathode at a first value (for example -0.2 V) which is selected so as to be between the potentials at which the metals begin to deposit under the conditions used, for a sufficient time to deposit pure noble metal,

(C) changing the potential applied to the cathode to a second value (for example -1.5 V) which is selected so as to be substantially more negative than the potential at which the less noble metal begins to deposit under the conditions used, the potential being increased until the total current density is higher than the limiting current density for the more noble metal so that the percentage of more noble metal in the less noble metal layer approaches zero, thereby permitting deposition of less noble metal, the potential being applied for a sufficient time to deposit a thickness of the less noble metal; and

(D) repeating step (B) and (C) for a predetermined number of cycles to obtain a corresponding number of layers of the metals.

5.3 D1 pertains to the technical field of the electrodeposition of metals. D1 (see page 133, left-hand column, second section to right-hand column, second line) mentions that the data resulting from investigation about the feasibility of depositing copper-nickel composite from a single electrolyte suggest that layered copper-nickel
deposits can be produced from a single electrolyte by modulating the deposition potential, with the relative thickness of the individual layers being controlled by the plating time at each potential.

5.4 Even if the person skilled in the art could be encouraged by the indication in D1 (see page 130, right-hand column, second section) that the distinction between micro- and macro-modulated layers is somewhat arbitrary (although the difference in thickness between the macro-modulated layers deposited according to the examples of D1 and the micro-modulated layers according to the definition given in D1 is of two orders of magnitude) to try applying the purely theoretical teaching of D1 for electrodepositing from a single electrolyte very thin (< 9nm) alternate layers of metals, he would not find in D1 any information as to how the suggested method could be used for producing such thin layers of substantially pure metals.

5.5 The skilled person could and probably would then refer to the teaching of D2, which pertains to the same technical field and is mentioned in D1 (see page 130, left-hand column, first section, last sentence; page 131, left-hand column, second section, first sentence), for its one-bath electroplating method.

5.6 However, D2 (see page 1988, left-hand column, last section, first sentence) describes mainly experimental results demonstrating the feasibility of electroplating cyclic multilayered alloys (CMA) structures of Ag-Pd alloy coatings from a concentrated chloride bath, but does not provide any definite teaching concerning other CMA alloys.

5.7 Indeed, D2 (see page 1993, right-hand column, lines 7 to 12) mentions that it is anticipated that cyclic multilayered alloys (CMA) Ag-Pd structures with layer
thickness < 10 nm may be obtained. However, it is to be noted that said result would be obtained, according to the same text location of D2, by decreasing the ion concentrations by about an order of magnitude, and thus by selecting a bath composition wherein, contrarily to the features of present Claim 1, the concentration of the less noble metal ion would not be near the level of saturation thereof at room temperature and thus, as stated in the present application (see page 5, second section, last sentence; see also page 7, last sentence), the deposited less noble metal would not be substantially pure; in this respect, the Appellant’s arguments that the much higher concentration of the less noble metal compared to the concentration of the more noble metal has the advantage that the less noble metal does not have a limiting current density, is considered as credible in view of the equation at the bottom of page 5 of the present application, mentioned in paragraph 3.1 above. Moreover, according to the same text location of D2 (see also page 1988, left-hand column, third section, second sentence), this step of decreasing the ion concentrations in the electrolyzing bath would result in an increase of erratic fluctuations in composition and morphology of the growth interface.

5.8 Thus, the Board is of the opinion that, taking into account

- the limited relevance of D2 for the electrodeposition of a composite foil consisting of substantially pure layers of one metal alternating with substantially pure layers of another metal, and

- the drawbacks mentioned in D2 arising from the electrodeposition of thin layers,

the person skilled in the art would not be incited to combine the teaching of D1 and D2 and,
even when trying to combine said teachings, would decrease the ion concentrations and thus would not arrive at the method of present Claim 1.

5.9 Therefore, the Board is of the opinion that the subject-matter of Claim 1 implies an inventive step in the sense of Article 56 EPC and that, thus, Claim 1 is allowable (Article 52(1) EPC).

The dependent Claims 2 to 7 are allowable by virtue of their dependence on allowable Claim 1.

6. Since the European patent application and the invention to which it relates meet the requirements of the Convention, a patent may be granted (Article 97(2) EPC).

Order

For these reasons, it is decided that:

1. The decision under appeal is set aside.

2. The file is remitted to the first instance with the order to grant a patent on the basis of the following documents, annexed to the official communication dated 15 January 1992:

   Description: Pages 1 to 11, and

   Claims: Nos. 1 to 7.

The Registrar: P. Martorana

The Chairman: E. Turrini

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