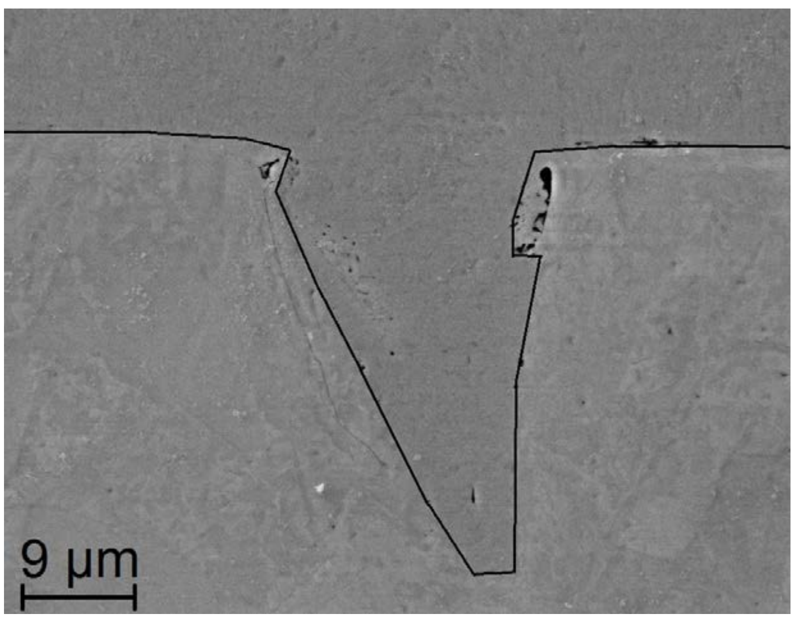
Feasibility study:
Development of localized electrochemical deposition for re-manufacturing



Project within ”Fordonsstrategisk Forskning och Innovation (FFI) -Hållbar produktion”

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FFI

Content

FFI in short

FFI is a partnership between the Swedish government and automotive industry for joint funding of research, innovation and development concentrating on Climate & Environment and Safety. FFI has R&D activities worth approx. €100 million per year, of which half is governmental funding. The background to the investment is that development within road transportation and Swedish automotive industry has big impact for growth. FFI will contribute to the following main goals: Reducing the environmental impact of transport, reducing the number killed and injured in traffic and Strengthening international competitiveness. Currently there are five collaboration programs: **Vehicle Development, Transport Efficiency, Vehicle and Traffic Safety, Energy & Environment and Sustainable Production Technology.**

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1. Executive summary

During the feasibility study, different approaches to perform localized electrochemical deposition (LECD) were investigated to determine if they can be applied in the context of re-manufacturing of industrial parts (local repair of surface damage). Three concepts were chosen to be further tested during the project. In the first concept, a microanode was used. By placing the microanode very close to the surface, local deposition can be achieved. The second method was to confine the electrolyte to a surface area by filling a small cylinder with the electrolyte and place it over the desired location. The third technique made use of so-called liquid marbles. A drop of electrolyte was first encapsulated in metallic powder and afterwards placed at the desired location. When approaching a microanode and applying a potential, the marble will collapse and a deposit consisting of the elements from both the electrolyte and the metal powder will be achieved.

The three concepts were tested and adjusted to achieve the best possible coatings. The confined bath method was found to work best. Good quality coatings with sub-microcrystalline microstructure and random crystal orientation were achieved. This concept was then used on a surface damage of a few microns in width and depth. The surface damage (scratch) could be filled with material, which means it was repaired successfully. It was also possible to pulse-electrodeposit material using the confined bath method. In a first attempt, the microstructure of the deposit was sub-microcrystalline. However, optimization of the plating parameters should allow to produce nanocrystalline deposits. That means that much harder deposits could be attained which would be beneficial for re-manufacturing.
The obtained results show clearly, that it is possible to repair surface damages by use of LECD. Hence, the aim of the feasibility project is accomplished and the long-term aim of saving resources in form of energy and material and help to avoid additional machining operations and/or annealing treatments in manufacturing of parts seems to be reachable.

2. Background

Electrodeposition is a reliable and economical method for producing thin coatings and free-standing structures [e.g. El-Sherik and Erb, Journal of Materials Science 30 (1995) 5743]. By controlling the process parameters such as pH value, current density, deposition temperature, duty cycle, bath composition, etc., structure and properties of the achievable material can be tailored [e.g. Schüler et al., Acta Materialia 61 (2013) 3945]. This has led to the development of nanocrystalline metals, alloys and metal-matrix composites which show exceptional properties with respect to strength and hardness as well as wear and corrosion resistance as illustrated in Fig. 1 [Robertson et al., Nanostructured Materials 12 (1999) 1035]. For example, by replacing conventional nickel with electrodeposited nickel of 10 nm grain size (Fig. 1a), an improvement in yield strength of more than one magnitude can be obtained [El-Sherik and Erb in “Nickel-Cobalt 97 – Vol. IV, Applications and Materials Performance”, The Metallurgical Society of CIM, Montreal, (1997) 257].

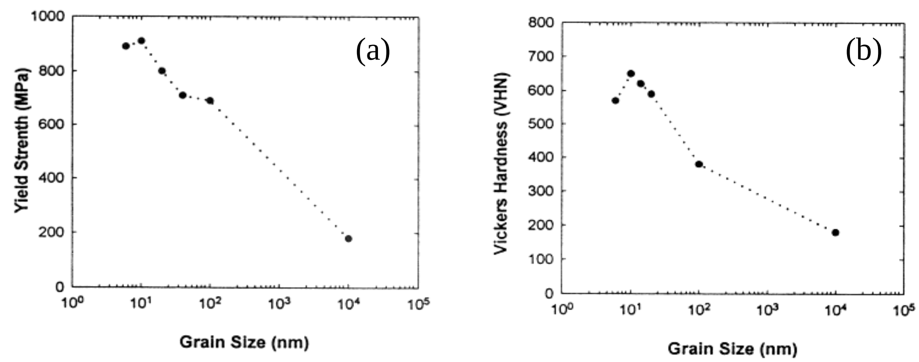

Figure 1: Grain size dependence of Vickers hardness and yield strength of nickel at room temperature [El-Sherik and Erb in “Nickel-Cobalt 97 – Vol. IV, Applications and Materials Performance”, The Metallurgical Society of CIM, Montreal, (1997) 257].

Nanocrystalline Co-P coatings, for example, can be used as hard chrome replacement (plating of hard-chrome is more and more restricted because of the formation of hexavalent chromium oxide during production which is a well-known carcinogen) [REACH regulation on webpage of the European Chemicals Agency (ECHA): http://echa.europa.eu/web /guest/regulations/reach/candidate-list-substances-in-articles]. In addition to the health and environmental aspects, the plating costs of nanocrystalline Co-P are reduced over hard chrome and corrosion and wear performance are improved [e.g. http://integran.com]. Moreover, nanocrystalline coatings can also be used to give strength to lightweight materials resulting e.g. in the replacement of metallic parts with lighter, more durable nano-coated structural plated plastics [e.g. Lausic et al., Journal of Sandwich Structures and Materials 16 (2014) 251].

In addition to coatings and free-standing structures which have a thickness between a few micrometers and several millimeters, localized electrochemical deposition (LECD) techniques are under development. LECD is mainly used to grow micron-sized features such as micropillars, microcolumns and microhelices [e.g. Pané et al. Electrochemistry Communications 13 (2011) 973]. When performing LECD to allow the growth of a metallic microfeatures, a microanode is used in an electroplating bath. As illustrated in Fig. 2, the deposition starts from a localized area on the cathode and the microfeature grows up towards the microanode in a controlled manner.

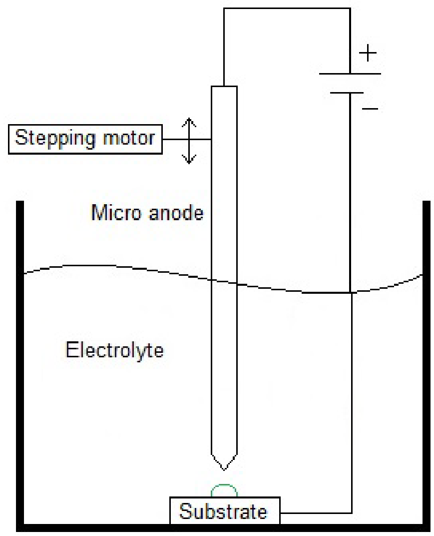

Figure 2: Scheme of the LECD experimental setup as used for deposition of microfeatures.

3. Objective

At the end of the feasibility study, sufficient knowledge should have been achieved to evaluate if LECD is a potential method for localized treatment in the context of re-manufacturing of industrial parts.

4. Project realization

This feasibility study performed together with Volvo Trucks (Volvo Lastvagnar AB) aimed at extending the application range of electrodeposition by developing local electrochemical deposition for re-manufacturing purposes. This would allow to save resources in form of energy and material and help to avoid additional machining operations and/or annealing treatments. The study included a literature study to provide an overview of different LECD concepts and electrolyte solutions, as well as the test of selected techniques by use of simplified setups. Hence, material with nano- or sub-microcrystalline microstructure was to be deposited on flat substrates and local surface defects like hollows/craters, but without immersing the actual substrate/part in an electrolyte.
The experimental verification of LECD did not include property characterization of the plated material and how scanning over the surface would be realized; neither was expected that the deposition technique would be optimized within the timeframe of the project.

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5. Results and deliverables

The literature study was performed in search for different approaches to perform LECD. Afterwards, the approaches were assessed if they can be applied in the context of re-manufacturing of industrial parts (local repair of surface damage) and within the set timeframe. Three concepts were chosen to be tested in simplified setups, i.e. the application of a microanode, the confined bath concept, and the use of so-called liquid marbles. In all three concepts the process parameters were adjusted to achieve best possible deposits at sufficient growth rates. The same nickel sulfamate electrolyte was used in all cases which had previously been employed for pulse-electrodeposition of nanocrystalline materials. The electrolyte must be carefully selected and adjusted for each application and was therefore not in focus of the study.

<u>Use of microanode</u>

In literature, a microanode is the most frequently used approach to achieve LECD. By placing the microanode very close to the surface, local deposition can be achieved. Hence, in the experiments, the distance between microanode and substrate, current density, and deposition time were varied to optimize the deposit quality. Thickness and quality of the achieved deposits were however not satisfying. Moreover, as can be seen in Fig. 2, the microanode concept is still using an electrolyte bath in which the substrate/part is submerged in. Hence, the attempt was made to confine the electrolyte bath around the microanode.

<u>Confined bath concept</u>

To confine the electrolyte bath, a small container filled with electrolyte was used (Fig 3a). The setup required a dense fitting of the container to the substrate and/or a more viscous electrolyte. A rubber sealing ring was used for preventing leakage and providing suction. However, for the sake of testing, a stage was altered so that the container could be screwed on top; the substrate was placed at the bottom and the rubber sealing ring provided tight fitting and acted as confinement (opening of 6 mm)). The setup is shown in Fig. 3b. Another solution allowing tight fitting has to be developed when the confined bath concept is to be used in future and the plating setup is supposed to be moved across the surface of the part.

In the confined bath setup, the volume of the cylinder is so small that the ions in the electrolyte get depleted after a few minutes, i.e. the electrolyte needs to be exchange regularly. From the examples shown in Fig. 4 it is evident that changing the electrolyte had a profound effect on the quality and thickness of the deposit. Also pitting could be averted by adjusting the current density.

An advantage of the confined bath concept is the possibility to perform pulsed electrodeposition which could result in smaller grain sizes and lead to nanocrystalline deposits. Two tests were performed (Fig. 5), with a pulse on-time of 10 ms and 1 s, respectively.

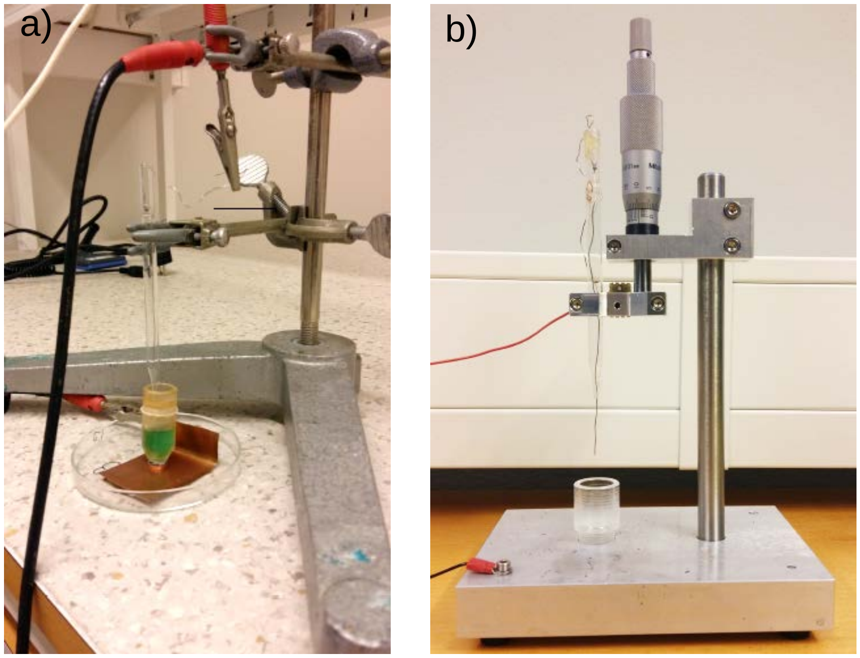

Figure 3: Experimental setup used in the confined bath concept: a) container placed directly onto the substrate (use of rubber sealing *ring), b) container screwed onto the stage (use of rubber sealing ring, a partly encapsulated microanode is mounted).*

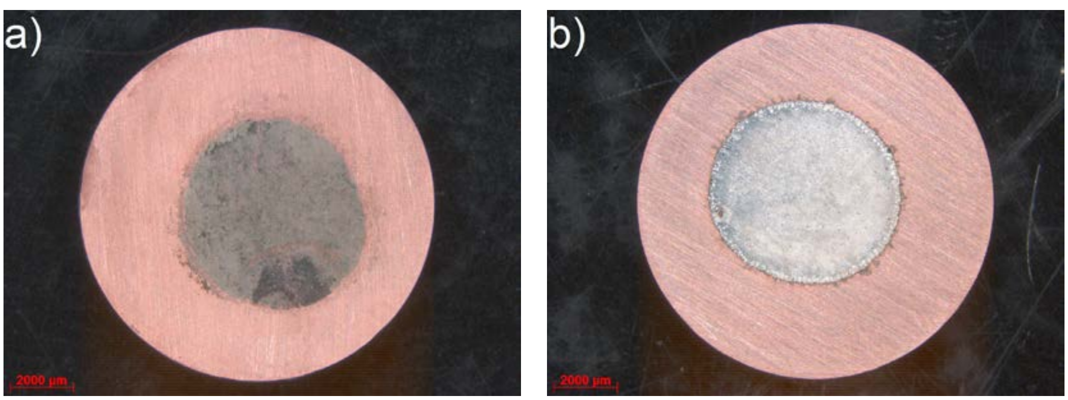

Figure 4: The effect of exchanging the electrolyte on deposit quality: a) no exchange of electrolyte, and b) with exchange of electrolyte.

Thickness and roughness of the deposits were measured. As expected, the deposit produced with constant current has the highest growth rate and is therefore thickest. As determined by electron backscatter diffraction (EBSD) technique, the deposits produced at constant current and by pulse-plating with pulse-on time of 1 s showed very homogeneous microstructures with sub-microcrystalline grain size (<500 nm). Hence, for achieving a nanocrystalline deposit, the pulse-plating parameters would have to be optimized further.

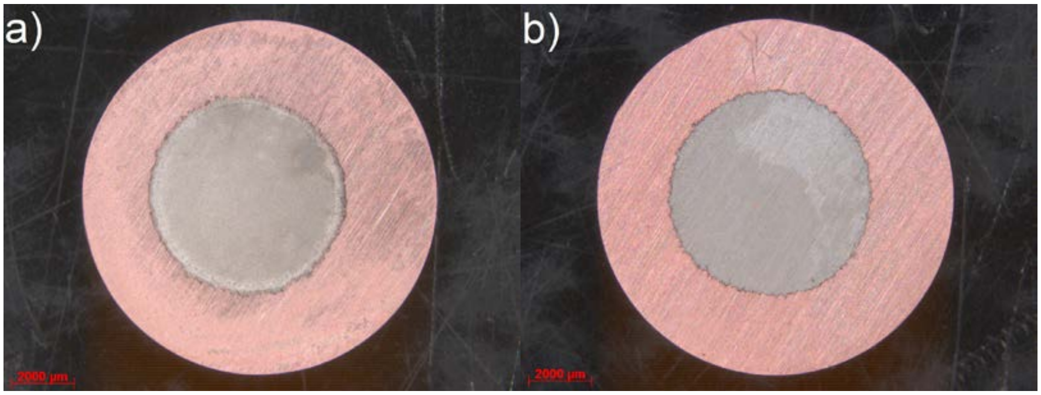

Figure 5: Deposits achieved by pulsed electrodeposition in a confined bath setup: a) pulse on-time of 10 ms, and b) pulse on-time of 1 s.

Several surface damages of different sizes were created, e.g. indentations and scratches. As can be seen in Fig. 6, a scratch was successfully filled with deposited nickel using the confined bath concept (constant current). EBSD analysis revealed that the grain size in the repaired scratch varies between 100 nm and ~1 µm (Fig. 7a). In the neighborhood of the scratch the grain size of the deposit is fast increasing in the growth direction, i.e. away from the interface, as can be seen in the orientation map given in Fig. 7b. The locations of the EBSD orientation maps are marked in Fig. 7a (not necessarily in the right size). A small grain size in the scratch is expected to be advantageous with respect to hardness and strength. Even though the microstructure is not nanocrystalline, the results are promising for being a first attempt.

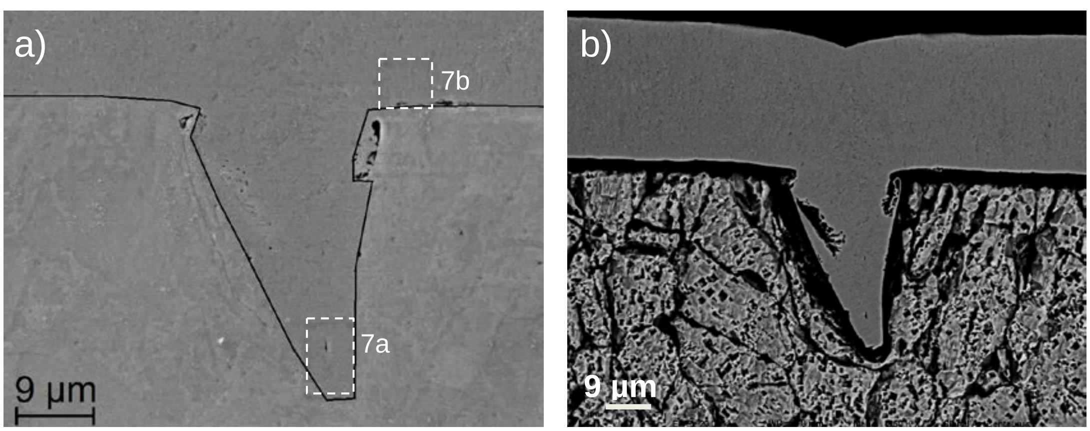

Fig. 6: Cross-section optical micrographs of a scratch repaired with LECD of nickel: a) without etching (a black line is added to visualize the interface; the locations of the EBSD orientation maps (Fig 7) are marked but are not in the right size), and b) overview with heavily etched Cu-substrate.

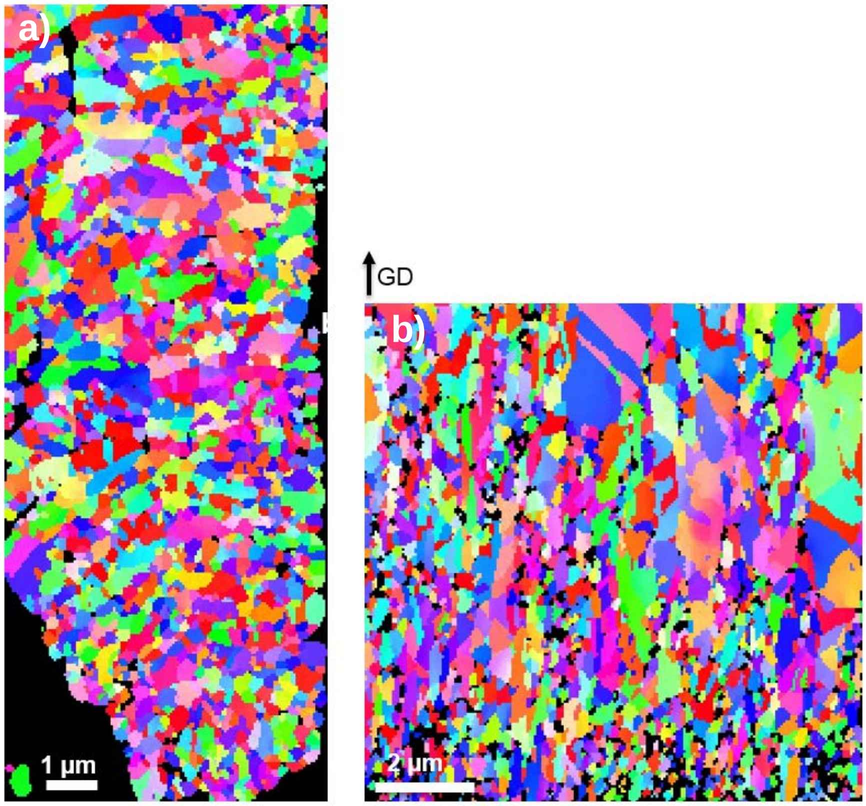

Fig. 7: EBSD orientation maps of the deposit as marked in Fig. 6a: a) in the tip of the scratch (maximum noise control applied), and b) in the neighborhood of the scratch.

Liquid marbles

By placing a drop of an electrolyte on a bed of hydrophobic metal powder, a liquid marble can be created [Shailendar and Sundaram, Materials and Manufacturing Processes 31 (2016) 81]. By moving the droplet, the powder will cover the surface of the droplet and encapsulate it. Afterwards, the liquid marble can be moved to the location of interest. When a microanode is approached and a potential applied, the marble will collapse and a deposit consisting of the elements from both the electrolyte and the metal powder will be achieved. Even though the procedure of picking and placing liquid marbles was repeated, this did not result in deposits of significant thickness.

5.1 Delivery to FFI-goals

The results show that it is possible to repair surface damages by use of LECD. Hence, the aim of the feasibility project is reached and the long-term aim of saving resources in form of energy and material and help to avoid additional machining operations and/or annealing treatments in manufacturing of parts may be reachable. The concept of using a confined bath was found to work best; it also allows to perform pulse-electrodeposition. Good quality coatings with (sub-) microcrystalline microstructure and random crystal orientation were achieved. A nanocrystalline deposit would be much harder and beneficial for re-manufacturing. Hence, the method still needs further optimization for the desired application area and the ability to repair surface damage of different sizes and shapes. There is still the option to make the electrolyte more viscous (e.g. use of a gel that is infiltrated with electrolyte) to overcome difficulties with leakage. However, this would also slow down the plating process and may not be acceptable in an industrial application.

6. Dissemination and publications

6.1 Knowledge and results dissemination

- Increased knowledge about LECD which can be applied in other context/projects.
- Different concepts have been tested.
- MSc thesis (Sebastian Proper) – see below

6.2 Publications

- MSc thesis by Sebastian Proper, Uppsala University (thesis work was performed at Chalmers under the supervision of U. Klement)

7. Conclusions and future research

The results show clearly, that it is possible to repair surface damages by use of LECD. Hence, the aim of the feasibility project is reached and the long-term aim of saving resources in form of energy and material and help to avoid additional machining operations and/or annealing treatments in manufacturing of parts may be reachable. The concept of using a confined bath was found to be best solution. Since the confined bath method allows to perform pulse-electrodeposition, local deposition of nanocrystalline material can be envisaged.

This positive outcome of the feasibility study opens up to continue the development work (probably in a larger consortium) towards a future industrial implementation trough a larger R&D project within the framework of FFI or other funding schemes. Aim of such a project would be to realize scanning and local deposition on the surface of a part. This would also include optimization of the plating process as well as detailed characterization and property evaluation of localized electrodeposits.

8. Participating parties and contact person

Contact person: Prof. Uta Klement