

Atmospheric plasma spraying of electrodes for conversion of electricity to hydrogen by high temperature alkaline electrolysis of water

Peter Tommy Nielsen, Troels Mathiesen, Jens Klæstrup Kristensen, Lisbeth Hilbert, FORCE Technology Denmark
Lars Yde, HIRC / DK

Energy obtained by wind turbines can be foreseen to constitute a significant part of the future energy sources. A major challenge is however the large variation over time in wind energy production. Energy conversion from electricity to storable energy is therefore a key technology to master, and it is therefore important to develop compact, reliable, cheap and energy efficient equipments for this.

An obvious solution is production of hydrogen based on water alkaline electrolysis. In the work presented the atmospheric plasma spraying (APS) of Raney nickel (50/50 Ni/Al) was used to develop electrodes with a large specific surface area as well as a considerable energy efficiency in high temperature water alkaline electrolysis. The coating process was analyzed using a plume analyzer as the primary tool and the coating properties were analyzed by a combination of bonding strength measurement, optical (OM) and scanning electron microscopy (SEM) as well as testing of the activated electrodes in a laboratory electrolysis cell. The results of the spraying process analysis are reported together with the electrochemical properties of the activated electrodes, and with regard to energy efficiency very positive results are obtained for the measured overvoltage.

1 Introduction

The modern society is totally dependent on huge quantities of energy that is used by the industry, for house heating and/or air-conditioning, for transportation of persons and goods as well as for many other purposes. This energy consumption has furthermore been steadily increasing since the beginning of the industrialization and today it on a worldwide basis constitutes several tons oil equivalent (toe) per inhabitant albeit very unevenly distributed between the various parts of the world. Fossil energy constitutes the major part of the consumption and it is now internationally recognized that this situation must be changed within the next few decades in order to limit the growth of the green house gas CO₂ in the atmosphere. Many energy resources as e.g. oil and gas seems furthermore to be limited in size so that an energy shortage is foreseen also for this reason, if other energy sources do not come into play.

The solution to the above challenge are manifold, but wind energy is a major player in this connection and energy obtained by wind turbines can therefore be foreseen to constitute a significant part of the future energy sources. A significant challenge in this connection is however the large variation over time in wind energy production. Energy conversion from electricity to storable energy is consequently a key technology to master, and it is important to develop compact, reliable, cheap and energy efficient equipments for this. An obvious way of temporarily storing this surplus electric energy is the conversion of water to Hydrogen and Oxygen by electrolysis followed by storage of the Hydrogen for later use in e.g. fuel cells. Other possible uses of the Hydrogen do also exist as it for example may be added to an already existing natural gas distribution system or converted to liquid fuel.

Existing equipments for electrolysis of water are quite large and in addition the energy efficiency is low. For the future effective electrolysis of water it is therefore necessary to develop energy and area efficient electrodes for such equipment. This calls for electrode surfaces that at the same time have a large exposed specific surface area and consist of materials that act as a catalyst for the Hydrogen or Oxygen production. Raney nickel (50/50 Ni/Al) is a potential material that may fulfill these requirements as it as-produced contain aluminum-nickel intermetallic phases that may be etched away during a so-called activation process resulting in a highly porous structure. Cheap and efficient ways of producing Raney nickel covered electrodes are of course also requested and in the work presented here the atmospheric plasma spraying (APS) of Raney nickel was used to develop electrodes with a large specific surface area as well as a considerable energy efficiency in high temperature water alkaline electrolysis.

2 Experimental

2.1 Coating Equipment

To produce test samples and full-size electrodes, Commercially available APS equipment was used. Initially the manual controlled and thereby the operator depended 7MC was used for APS in the preliminary spray testing. But the actual parameter scan and adjustment was conducted with a state of the art Sulzer Metco multicoat system for the APS. This system enables full parameter control and recipe locking, which can utilize screening of the effect of single and combined parameter adjustment.[5,6]

The APS systems used the simple and reliable 3M torch, that was mounted on a robot programmed for x,y motion.

As spray qualification a Spray Watch 3i plume analyser was used combined with the knowledge from the Ni-Al phase diagram, as the material can be problematic to spray using the plasma process. This also contributed to minimise material waste and shorten the magnitude of trials. [3,4]

The substrate for the test specimens was pure nickel, 0.5 mm thick, and with a diameter of 32 mm. A special fixture was developed in such a way that only a spot, diameter 10.5 mm, would be coated. This was done to meet the specification of the electrochemical measuring setup. The thin nickel substrate is relatively soft and is easily deformed, which is not tolerated in the final product. A careful approach concerning the pre-treatment of the substrate was examined and developed to exclude deformation of the electrodes.

As a result of achieved coating optimisation, specially designed electrodes with a surface area equivalent to 600 cm² were coated. These electrodes were tested under final product conditions. Both zero gap - solid nickel substrate, and non zero gap - mesh metal nickel substrate, design were tested. The definition of zero gap and non zero gap relates to the distance to a special component in the operating hydrogen development cell.

All tests and analyses concerning plasma spraying and electrochemical tests were conducted at FORCE Technology, Denmark. The full-size electrode testing was conducted by Green Hydrogen, Ikast.

2.2 Spray Powders

Initially a gas atomised NiAl50 powder was tested in two non specified particle sizes. They were only defined as very fine and very coarse. These powders were used in the preliminary testing, that resulted in this investigation using a particle size interval -90~+45 µm. Cross section of powder is shown in figure 2.1 The powder was applied by APS on both anode and cathode side of the electrode.

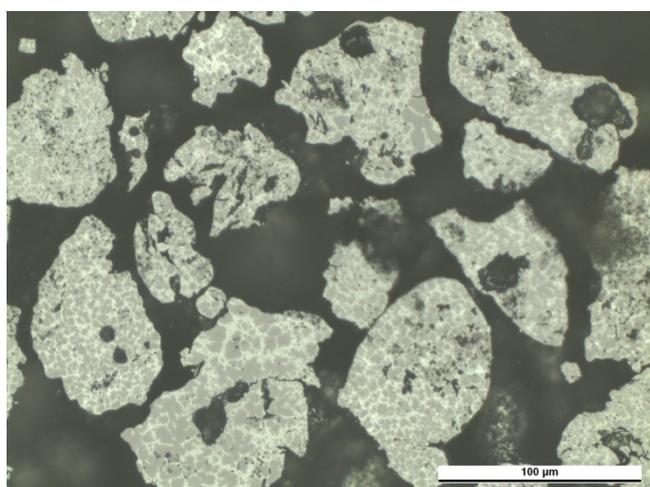


Fig. 2.1 Cross-section of NiAl powder used for tests.

2.3 Activation

The as-sprayed NiAl is a fairly compact coating with few pores and cracks. In order to activate the coating, the specimens were exposed to 30% KOH containing 10 wt.% K-Na tartrate-tetrahydrate at 80 °C for 24 hours. This treatment leaches out aluminum from the intermetallic phases and results in a highly catalytic sponge-like structure of nickel. Cross-sections of coating before and after activation are shown in Fig 2.2.

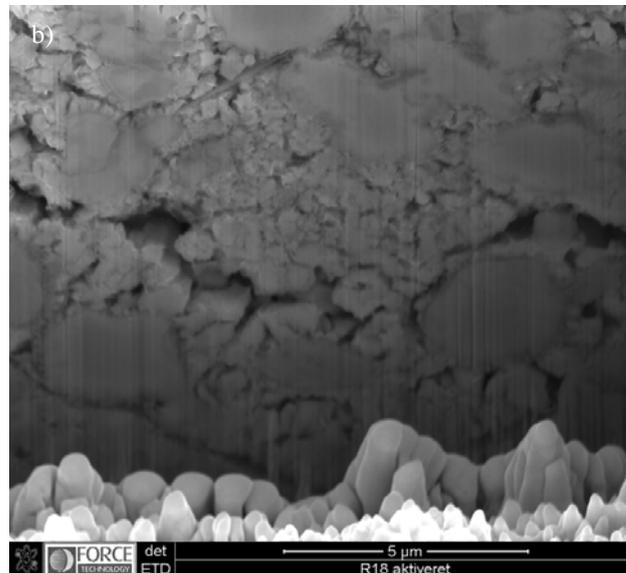
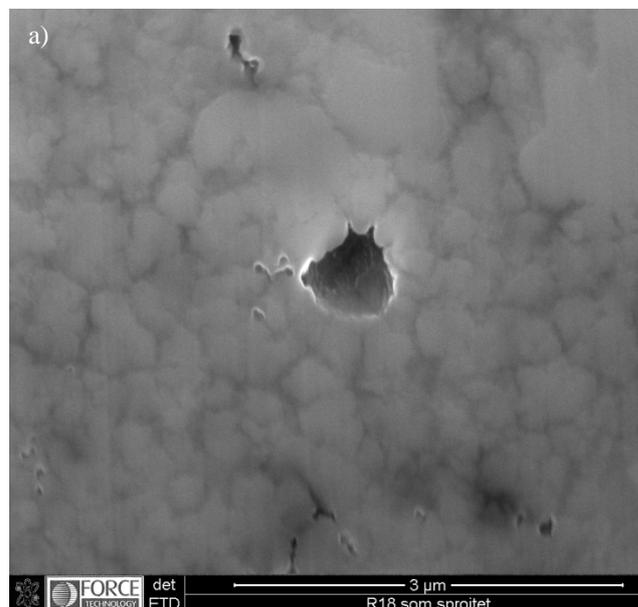


Fig. 2.2 SEM pictures of cross-sections made by focused ion beam technique (FIB). As-sprayed (a) and activated NiAl coating (b).

2.4 Electrochemical Measurements

In order to screen candidate APS coatings for their efficiency to hydrogen electrolysis, an electrochemical testing method was established. The approach is

comparable to that previously used by Schiller to allow comparison [1,2].

The disc specimens were mounted in a holder that restricts exposure to the coating at the centre ($\varnothing 11$ mm, 1 cm^2). Testing was performed in a three-electrode cell consisting of a nickel counter electrode and a mercury/mercury oxide reference electrode. The other cell components were made from alkali resistant polymers. The test solution was 25% KOH maintained at $70 \text{ }^\circ\text{C}$ throughout the test. All measurements imply IR compensation based on current interrupt.

The test cycle involved galvanostatic conditioning at -10 and -200 mA/cm^2 and for 2 and 14 hours, respectively. Subsequently, a galvanodynamic scan was performed from 0 to -300 to $+300 \text{ mA/cm}^2$ at a scan rate of $0.1 \text{ mA/cm}^2/\text{s}$.

3 Results and Discussion

3.1 Coating Properties

The NiAl powder exhibited very good flow ability when exposed the Hall Flow meter test. Therefore a stable APS process was easily achieved. The real challenge was to minimise the heating of the NiAl powder, as the Aluminum has a tendency to burn rapidly. Also in the opening test a clear green spray plume was identified indicating the formation of Nickel oxide. A spray parameter adjustment to stabilize the plume and lower the amount of oxides was carried out, and formed the point of origin for the following parameter scan using the Spray Watch 3i plume analyser. [4]

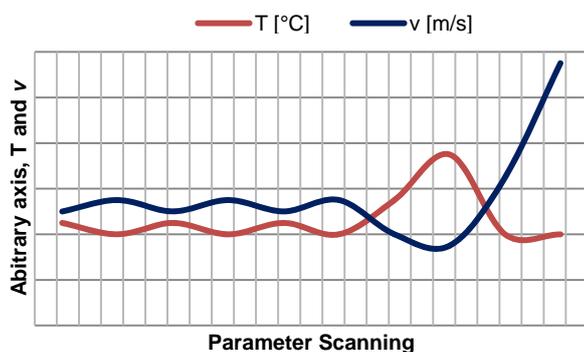


Fig. 3.1 Behavior of the NiAl particle temperature and velocity in the APS process undergoing parameter scanning

As illustrated in figure 3.1 it is not possible reduce the temperature significantly, which can in some extent be related to the measuring technique of the plume analyser. An increase of the particle temperature is possible, but not desired. Indirectly the temperature was lowered by increasing the particle velocity. This was achieved by parameter scanning, but the drastic

increase came from change of nozzle design. The measured values with relation to parameters are listed in table 3.1

NiAl powder	T [$^\circ\text{C}$]	v [m/s]
Coarse non-specified $-90 \sim +45 \mu\text{m}$	2550	126
	2460	125
Change of nozzle	2250	360

Parameter	Before	After
I [A]	400	600
U [V]	65	65
Primary gas (Ar) [STLM]	43	50
Secondary gas (H_2) [STLM]	12	6

As a direct result of these maneuvers the deposition efficiency was improved significantly. The material consumption was initially 69 g/min and there after reduced to 25 g/min , i.e. a reduction equivalent to 74% of the NiAl consumption when producing the electrodes.

The coating bonding to the substrate was in parallel to the parameter scanning measured using a simple pull of tester. As the nickel is relatively soft and the coating exhibits brittle properties, the adhesion was tested continuously on steel. The final measurements were conducted by gluing nickel to steel, and thereby preventing deformation of the nickel substrate. The maximum measured glue strength was 57 MPa , and this bar was passed by the coating adhesion.

When the best obtainable adhesion and distribution was achieved, the influence of the coating thickness was evaluated.

As the desired coating has a large surface area, a thick coating with a secondary structure, typically considered coating defects, such as cracks and porosity are positive in this specific application. However, as the coating thickness increases, the adhesive strength between coating and substrate decreases to an extent in a ratio not usable when the coating is activated.

Other parameters such as movement of the torch and stand-off had substantial influence on the coating properties. Especially the stand-off was a parameter to consider, as not only would it have effect on the coating but also on the somewhat heat sensitive and relatively thin substrate. A too short stand-off resulted in poor coating properties and comprehensive substrate deformation. In the other case where the distance is too long, the substrate was not affected negatively, however there were reduced bonding and

material changes caused by the prolonged heat exposure.

The window of the stand-off was discovered to be quite narrow, causing returning problems with substrate deformation, which initiated a study of the pre-treatment of the substrate handling. A major problem was the tension induced by blasting, which was released under the coating process and causing extensive deformation. A method of applying sufficient surface roughness to substrate with minimal adding of tension and deformation was examined. The approach was as illustrated at figure 3.2.

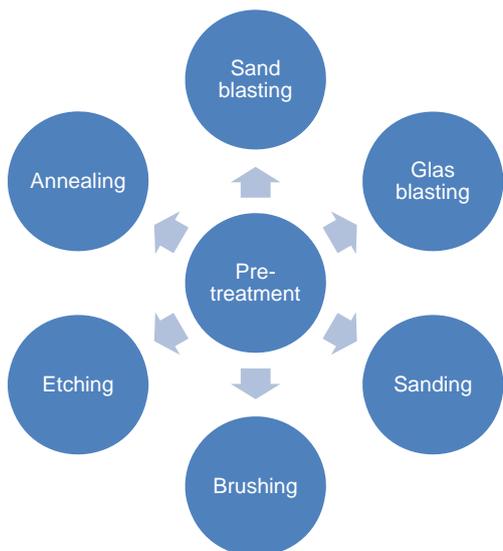


Fig. 3.2 The examined ways to obtain suitable substrate properties.

The study suggested that the best results were obtained by combining annealing and sandblasting, when the considerations were minimum deformation and maximum adhesion. However sanding could be sufficient when mesh metal, as the substrate, was to be coated. The applied tensions in the mesh metal are more easily released without causing deformation. A simple bend test of the brittle coating on the soft substrate is shown in figure 3.3.

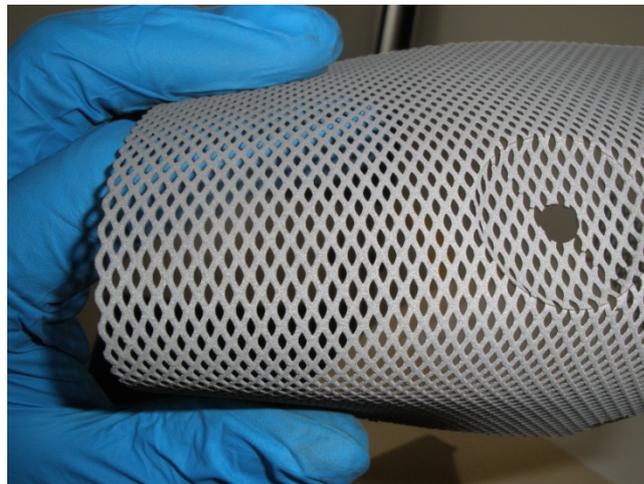


Fig. 3.3 Simple bend test of the coated electrode

3.2 Electrochemical Performance

The obtained electrochemical performance is shown in Table 3.2 as cell voltage calculated from the IR compensated potentials of hydrogen and oxygen evolution at a current density of 300 mA/cm².

Table 3.2 Electrode potentials and cell voltage of NiAl coatings in 25% KOH at 70 °C. The results are correlated with measurements of bare nickel plate.			
Surface	Hydrogen electrode potential at 300 mA/cm ² (V vs SHE)		
	n=1	n=2	average
Nickel (non-coated)	-1.270	-1.268	-1.269
NiAl (30µm)	-1.040	-1.050	-1.045
NiAl (100 µm)	-0.940	-0.933	-0.937
NiAl (300 µm)	-0.931	-0.931	-0.931
	Oxygen electrode potential at 300 mA/cm ² (V vs SHE)		
	n=1	n=2	average
Nickel (non-coated)	0.705	0.672	0.689
NiAl (30µm)	0.643	0.632	0.638
NiAl (100 µm)	0.618	0.601	0.610
NiAl (300 µm)	0.613	0.617	0.615
	Cell Voltage (V)		
	n=1	n=2	average
Nickel (non-coated)	1.975	1.940	1.958
NiAl (30µm)	1.683	1.682	1.683
NiAl (100 µm)	1.558	1.534	1.546
NiAl (300 µm)	1.544	1.548	1.546

Compared with non-coated nickel, the NiAl coatings immediately provide a considerable improvement (i.e. reduction) in cell voltage, even at a small coating thickness of 30 µm. A wide range of coatings produced by APS have been tested this way. The best performance is observed for a coating with 100 µm thickness. No additional improvement was observed by increasing the coating thickness further to e.g. 300 µm. The electrochemical performance is determined by a complex relationship between the applied spray parameters and the obtained microstructure. This relationship is not yet fully understood, but the tests show that very high efficiencies can be obtained for Raney nickel coatings deposited by APS. Further optimisation of the electrode surfaces is now going on.

It will include use of oxide-doped NiAl coatings for the anode.

Similar, but not standardised, measurement has been conducted comparing coated mesh nickel to non coated mesh metal. As show in figure 3.4 the cell voltage drop is significant at even low current densities.

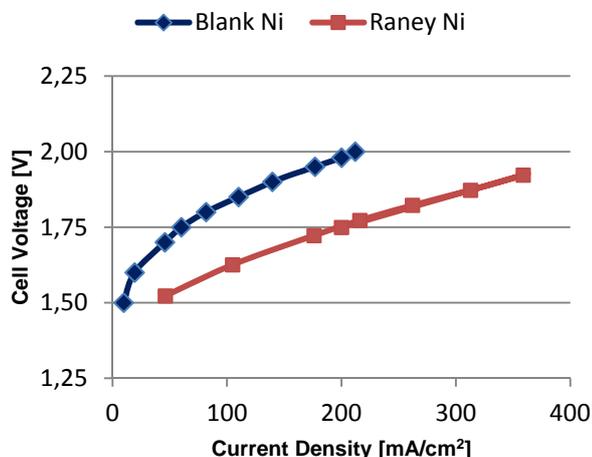


Fig. 3.4 Voltage comparison of NiAl coated and non coated nickel mesh metal.

4 Conclusions

This work has shown the possibility of using atmospheric plasma spraying to produce highly efficient electrodes for conversion of electricity to hydrogen by high temperature alkaline electrolysis of water.

The systematic screening of APS parameters using a plume analyser combined with analysis of bond strength, pre-treatment and stand-off resulted in non deformed 0.5 mm nickel plates with the a surface area equivalent to 600 cm². The bond strength of the coating was defined as minimum 57 MPa, when not activated. Furthermore the NiAl consumption was reduced by 74%.

The usage of mesh metal seems promising, as the preliminary electrochemical test indicate positive results. The manufacturing process of these electrodes was simplified showing excellent coating bond strength before activation.

The electrochemical tests have shown very promising results of the NiAl coatings as cathode when produced by APS. The obtained efficiency is comparable to or perhaps better than that obtained by Schiller who used the more complicated VPS process. Additional improvement of the cell voltage (1.55 V at 300 mA/cm²) obtained so far, can be expected when the anode side has been optimized further by using oxide-doped NiAl coatings.

5 Outlook

The performance of mesh metal and full size electrodes is undergoing tests and the results will indicate the point of direction for further analysis.

The test coatings containing cobalt oxide are not concluded. These tests could in all probability show a different mixture ratio to be convenient. Also a consideration of alternative oxides is an evident possibility

A thorough study of the adhesion and long term stability of the activated coating is needed. The approach could be to examine a gradient of the coating with Ni powder vs. NiAl powder, which influences the adhesion properties positively after activation.

The atmospheric plasma spraying process is highly production friendly and relatively inexpensive, so the combination of alternative coating approaches to manufacture an even better end product is apparent. This should be conducted with low cost substrate as the target.

6 Acknowledgement

This work is partially funded by the Energy Technology Development and Demonstration Program in the project "2nd generation Alkaline Electrolysis". The project partners, Risø DTU and Green Hydrogen, have contributed with professional feedback when needed.

7 Literature

- [1] Schiller, G. Henne, R. Mohr, P and Peinecke, V., High Performance Electrodes for an Advanced Intermittently Operated 10-kW Alkaline Electrolyser, Int. J. Hydrogen Energy, Vol. 23, No. 9, pp. 761-765, 1998
- [2] Schiller, G. Henne, R. and Borck, V., Vacuum Plasma spraying of High-Performance Electrodes for Alkaline Water electrolysis, JTTEE5, Vol. 4, No. 2, pp. 185-194, 1995
- [3] ASM Handbook Volume 3, Alloy Phase Diagrams, section 2, p. 49
- [4] Spray Watch 3i, www.oseir.com/
- [5] Sulzer Metco APS Multi Coat, www.sulzermetco.com
- [6] Metco 7 MC, www.sulzermetco.com