OPTIMIZATION OF THE RANEY NI COATING PRODUCTION PROCESS FOR CATALYSIS PURPOSES IN HYDROGEN GENERATION

***L.E. Sanz*[1], *B. Garrido*[2], *V. Albaladejo*[2], *I. Garcia Cano*[2], *J. Sánchez*[2]**

[1]lusaro96@gmail.com
[2]Centro de Proyección Térmica (CPT), igcano@cptub.eu

This investigation aims to develop and optimize a methodology for producing Raney nickel coatings for catalysis in Alkaline Water Electrolysis (AWE) using mechanical alloying and Cold Gas Spraying (CGS). Bimetallic Ni-Al powders were synthesized through planetary and attrition ball milling with varying Ni-Al ratios. The optimized powder was then deposited onto aluminum and steel substrates using CGS with different spraying parameters and nitrogen as the accelerating gas. Coatings formed on steel substrates underwent thermal treatment to study the effect of temperature and time on intermetallic phase formation. The planetary ball milling method was unsuccessful, resulting in poorly mixed particles, while the attrition ball milling produced a well-mixed powder. After optimization, the powder was successfully deposited on both substrates, maintaining its microstructure. Thermal treatment led to the formation of intermetallic phases, with a transition from Al-rich to Ni-rich phases observed as temperature increased.

Keywords: mechanical alloying, Raney nickel, cold spraying, coating, intermetallic, Ni-Al.

1. INTRODUCTION.

Hydrogen (H_2) is seen as a future fuel [1] as it offers a clean, emission-free alternative to fossil fuels, reducing carbon footprint and environmental impact. Currently, hydrogen production mainly relies on nonrenewable sources like natural gas, which emits significant greenhouse gases through the steam reforming process it undergoes. A more environmentally friendly method is water electrolysis, which splits water into oxygen (O_2) and hydrogen using electricity, with no greenhouse gas emissions [2].

There are four main types of water electrolysis technologies: Alkaline Water Electrolysis (AWE), Anion Exchange Membrane Electrolysis (AEM), Proton Exchange Membrane Electrolysis (PEM), and Solid Oxide Electrolysis (SOEC). This work focuses on AWE, which operates competitively at 70-90°C with electrodes made of porous nickel-coated stainless steel in an alkaline electrolyte of potassium or sodium hydroxide. The electrodes are separated by a diaphragm, typically asbestos or Zirfon, which prevents the mixing of oxygen and hydrogen while allowing hydroxide ion diffusion [2].

The main challenge for hydrogen production technologies is to increase production rates and lower costs to compete with nonrenewable sources. This can be addressed by enhancing the electrocatalytic activity of electrodes through better material selection, increasing surface area, and introducing more surface defects in nanostructured materials. Raney nickel, widely used in Alkaline Water Electrolysis (AWE), is produced by leaching aluminum from a Ni-Al alloy, preferably from aluminum-rich intermetallics like $NiAl_3$, Ni_2Al_3, and NiAl. These phases possess the fastest leaching rates, leading to a more porous and active nickel structure. The high surface area increases electrocatalytic activity, reduces overpotential for hydrogen evolution, and boosts the overall efficiency of water electrolysis [1,3].

These intermetallic Ni-Al phases are typically formed by heat treating coated substrates through a diffusion-based process, where aluminum and nickel atoms move until a specific atomic ratio is reached [3]. According to Fick's laws, this movement is driven by differences in composition within the coating, and higher temperatures increase atomic mobility by providing more energy. Maximizing the contact area between materials, such as with a lamellar structure, enhances diffusion. Mechanical alloying techniques can be used to produce powders with these characteristics for optimal diffusion.

Mechanical milling techniques are solid-sate powder processes where phenomena like cold welding and fracturing take place due to high impact energies between milling media and powder. These methods are commonly used to blend powders, reduce particle size, and induce reactions between materials. Mechanical milling can also produce nanocrystalline materials with grain sizes between 1-100 nm, characterized by a high fraction of atoms at grain boundaries. A higher volume fraction of surface defects, which arises from a higher fraction of atoms located on the electrolyte-electrode surface relative to the volume of each grain, can increase the electrocatalytic activity of the coating thanks to the more favorable electronic structure of the out-of-equilibrium atoms [5]. An ultrafine structure with this characteristic, which is highly desired for the Ni-Al catalytic surface for AWE, can be deposited by Cold Gas Spray (GGS).

Cold Gas Spraying (CGS) is a technique that accelerates powder particles using inert gases like nitrogen, argon, or helium at supersonic speeds, with temperatures between 300-1000°C, below the material's melting point. The particles impact the substrate at high velocities, causing plastic deformation and adhering through heteroepitaxy and adiabatic shearing. This process results in low porosity, low oxide content coatings that preserve the powder's composition and microstructure [6].

2. MATERIALS AND METHODS.

Commercially available Höganäs Amperit 175.001 nickel powder and Arasan Standard Super fine aluminum powder, both water atomized, were used as starting powders for this work.

A Retsch GmbH Type PM 400 fast planetary ball mill was employed, using several different parameter combinations, displayed in Figure 1, to mix both powders with the intention of obtaining a lamellar structure. A Union Process Model 01HD CE attritor ball mill was also employed, operating at low temperatures utilizing liquid nitrogen as coolant, with the same purpose. The parameters used in the attrition ball milling process are summarized in Table 1.

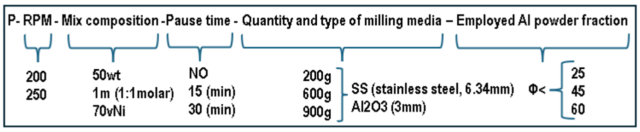

Figure 1. Parameters used in the planetary ball milling process

Table 1. Parameters used in the attrition ball milling process.

Powder	A1	A2
RPM	180	180
Time (h)	8, 16 (total)	8, 16 (total)
Media	3000g SS 6.34mm balls	3000g SS 6.34mm balls
Temp. (°C)	-120°C	-120°C (8h) -190°C (8h)

A set of CGS depositions was conducted onto aluminum and steel sheets using powder A1 (16h) as feedstock. The equipment used for this process was an Impact Innovations Gmbh Kinetiks 4000 high-pressure cold gas spray equipment, fitted with a water-cooled WC convergent-divergent nozzle, available at CPT laboratories. All samples were grit-blasted with G24 corundum (800µm grit size) at 0.5MPa. The highest spraying temperature is limited by the melting point of aluminum (65°C). Nitrogen was used as carrying gas. The combinations of controllable parameters are displayed in Table 2.

Heat treatments at temperatures comprised in between 450-600°C, maintained during 4-18h, were conducted on the as-sprayed coatings using a Carbolite GHA 12/450 controlled atmosphere tubular furnace. An argon flow through the furnace was employed to evacuate all oxygen thus allowing the process to be performed in inert conditions. Samples were placed inside the furnace at room temperature and allowed to cool, also inside the furnace, until room temperature was again reached. All parameters are summarized in Table 3.

Table 2. Parameters used in the CGS depositions.

Sample	C1	C2	C3	C4	C5
Substrate	Al 1mm	Al 1mm	Steel 1mm	Steel 1mm	Steel 5mm
Pressure (bar)	20	30	20	30	30
Temp. (°C)	300	650	300	650	650
Standoff (mm)	20	20	20	20	20
Traverse speed (mm/s)	100	100	100	10	40
Jump distance (mm)	0.75	0.75	0.75	0.75	1
Layers	1	1	1	1	1

Table 3. Parameters used in the heat treatment process.

Sample	H1	H2	H3	H4
Temp. (°C)	450	550	550	600
Time (h)	4	4	18	4
Temperature increase rate (°C/min)	10	10	10	10

Microstructural and elemental investigations were carried out using both a PhenomWorld BV Phenom ProX SEM, available at CPT laboratories, and a FEI Quanta 200 SEM, available at CCiTUB, both equipped with a backscattered electron (BSE) detector and an energy dispersive X-ray spectroscopy (EDS) system. Phase analysis was performed by X-ray diffraction (XRD) using a PANalytical X'Pert PRO MPD X-ray diffractometer. Patterns were processed with the PANalytical X'Pert HighScore Pluss 80 software. Particle size distributions were obtained by laser diffraction using a Beckman Coulter Multiwavelength LS 13 320 Laser Diffraction Particle Size Analyzer.

3. RESULTS AND DISCUSSION.

3.1. Assessment of Ni-Al powder production by planetary and attrition ball milling.

Electron microscopy observations of the as-milled powders produced by planetary ball milling revealed two distinct outcomes: either the powder retained the original rounded morphology of the commercially available starting materials, or it experienced excessive flattening, as shown in Figure 2. These outcomes were influenced by the aggressiveness of the milling process, which can be adjusted by modifying the parameters listed in Table 1. Despite multiple efforts to produce a powder with a lamellar structure and increased contact area between the materials, the desired outcome was not achieved using planetary ball milling.

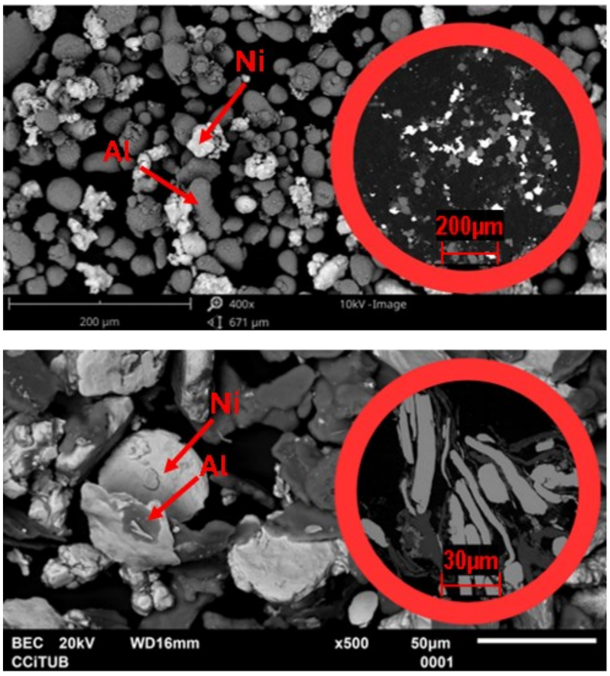

Figure 1. Powder produced through low-energy milling with 200g of 3mm alumina grinding balls (top) and 900g of 6.34mm stainless steel grinding balls (bottom).

Conversely, powder particles with the desired structure and size (A1) were successfully produced through attrition ball milling. Although A2 powder particles exhibited a similar structure, they were too small for the CGS process due to flowability issues. Figure 3 illustrates alternating layers of nickel and aluminum, with areas labeled 1 and 3 composed almost entirely of aluminum, and area 2 consisting primarily of nickel. The enhanced fracture phenomena, caused by embrittlement at low temperatures, facilitated a more intimate mixing of the two materials, resulting in the desired Ni-Al layered structure.

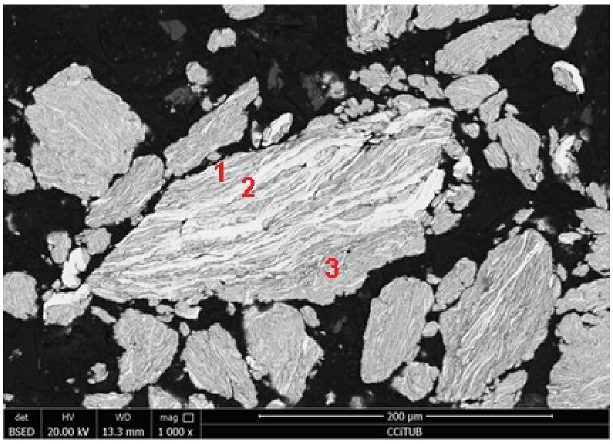

Figure 2. Powder produced (A1) via cryogenic attrition ball milling.

<u>3.2. Ni-Al coatings deposition by CGS: microstructure characterization.</u>

Coatings deposited on aluminum and steel substrates demonstrated notable differences in adhesion and continuity, as it can be noted in Figure 4. Aluminum substrates, being softer, exhibited better coating adherence, with significant plastic deformation upon particle impact, resulting in continuous coatings that conformed to surface irregularities. In contrast, coatings on steel substrates were discontinuous and poorly adhered, with significant longitudinal gaps between the coating and the substrate. The steel, being much harder, did not undergo the same level of plastic deformation at those process temperatures, leading to reduced material deposition and less uniform coatings. As expected from a low-temperature process like CGS, the microstructure of the powder was preserved in the coatings, and only little phase transformation occurred [6] (Table 4).

To address these challenges and achieve optimal coatings on steel—commonly used in alkaline water electrolyzers—process parameters were adjusted, ultimately resulting in an optimal coating for the C5 sample.

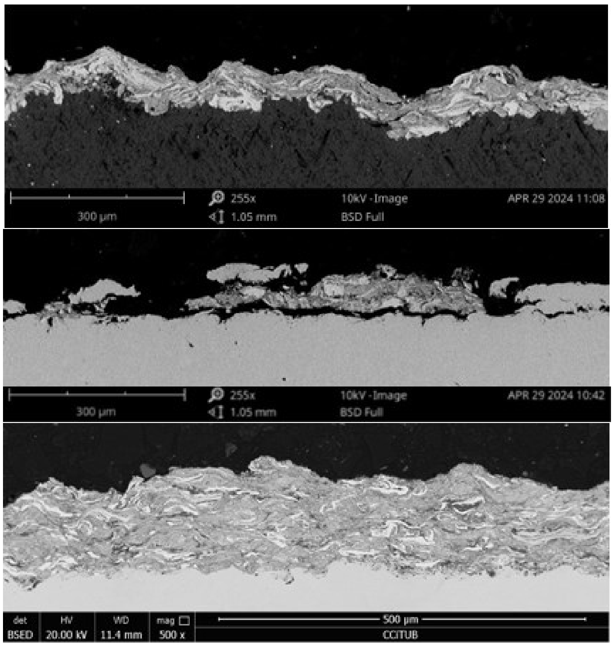

Figure 3. Different deposited coatings: C1 (top), C3 (middle) and C5 (bottom).

The contrast between the aluminum and steel coatings underscores the critical role that substrate material plays in the CGS process, highlighting the need for fine-tuned parameters tailored to the specific substrate-powder combination.

<u>3.3. Effect of thermal treatment on coating microstructure and phase composition.</u>

The XRD analysis of the thermally treated samples revealed significant phase transformations compared to the as-sprayed coating. After treatment at 450°C for 4 hours (H1), new peaks corresponding to $NiAl_3$, Ni_2Al_3, and Ni_3Al appeared, indicating the formation of intermetallic compounds. Semiquantitative phase analysis using the RIR method confirmed a reduction in Ni and Al content, as these elements formed intermetallic phases. Comparison of samples treated at 450°C and 600°C for 4 hours (H1 and H4, respectively) showed that the peaks for Al and $NiAl_3$ disappeared at the higher temperature, while Ni peaks remained. New peaks corresponding to NiAl appeared, and the Ni_3Al phase increased significantly.

A comparison of XRD patterns for samples treated at 550°C for 4 and 18 hours (H2 and H3) showed the presence of Ni, NiAl, Ni_2Al_3, and Ni_3Al in both coatings. However, additional peaks corresponding to iron and iron oxides were found in the H3 sample due to thinning of the coating during metallographic preparation.

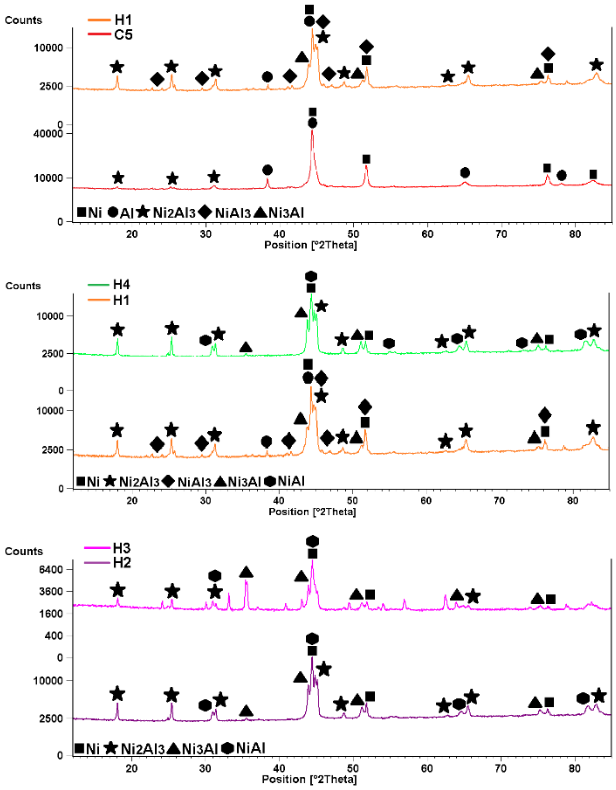

Figure 4. XRD patterns comparative.

Table 4. RIR semiquantitative phase analysis.

	Samples				
Phase	**C5**	**H1**	**H2**	**H3**	**H4**
Al (wt.%)	29	11	-	-	-
Ni (wt.%)	50	20	20	-	19
NiAl (wt.%)	-	-	25	-	27
$NiAl_3$ (wt.%)	-	25	-	-	-
Ni_2Al_3 (wt.%)	20	36	37	-	35
Ni_3Al (wt.%)	-	8	18	-	19

Backscattered electron images also revealed the development of porosity in thermally treated samples, observable in Figure 6, which increased with temperature and time. This was attributed to the Kirkendall effect, where the faster diffusion of aluminum into nickel leads to vacancy formation and subsequent porosity on the aluminum side of the diffusion couple [7].

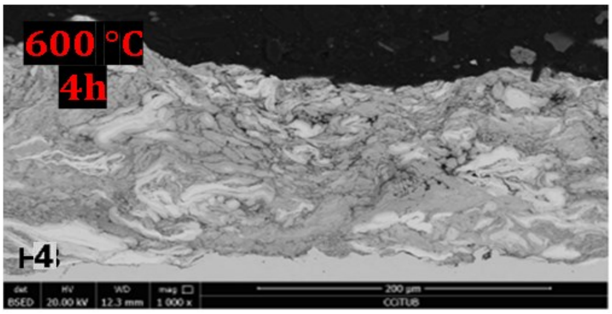

Figure 5. BSE image of the H4 heat treated sample.

4. CONCLUSIONS AND FUTURE WORK.

This study successfully developed an optimized method to produce bimetallic Ni-Al powder through mechanical alloying, which was then used to create coatings via Cold Gas Spraying (CGS). Thermal treatment resulted in the formation of intermetallic compounds in the coatings. Planetary ball milling was found ineffective for producing the desired Ni-Al powder due to inadequate particle fracture, while attrition ball milling under cryogenic conditions produced the ideal lamellar structure. The powders were effectively deposited on aluminum and steel substrates using optimized CGS parameters, resulting in dense coatings that preserved the material distribution of the original feedstock powder. Thermal treatment further induced the formation of Ni-Al intermetallic phases, with higher temperatures favoring Ni-rich phases.

Further studies on the catalytic activity of these coatings as Raney nickel surfaces in AEM electrolyzers could be assessed by studying the effects of chemical etching activation on microstructure and porosity, testing adhesion strength before and after etching, and evaluating electrocatalytic performance for hydrogen production.

5. REFERENCES

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