

PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE

SCHOOL OF ENGINEERING

# ANALYSIS OF THE MICROSTRUCTURE AND ELECTROCHEMICAL PROPERTIES OF Cu-Ni-AI USED FOR MOLTEN CARBONATE FUEL CELL

## CAMILA FERNANDA ARCOS SEGURA

Thesis submitted to the Office of Graduate Studies in partial fulfillment of the requirements for the Degree of Doctor in Engineering Sciences.

Advisors:

MAMIÉ SANCY CAROLA MARTÍNEZ

Santiago de Chile, March, 2024 © 2024, Camila Fernanda Arcos Segura



PONTIFICIA UNIVERSIDAD CATOLICA DE CHILE SCHOOL OF ENGINEERING

# ANALYSIS OF THE MICROSTRUCTURE AND ELECTROCHEMICAL PROPERTIES OF Cu-Ni-AI USED FOR MOLTEN CARBONATE FUEL CELL

## CAMILA FERNANDA ARCOS SEGURA

Members of the Committee:

MAMIE SANCY

**CAROLA MARTINEZ** 

**ARMELLE RINGUEDE** 

MAGDALENA WALCZAK

CLAUDIO AGUILAR

MICHEL CASSIR

SERGIO MATURANA

Tag datena Wat Claudio Aguilar Rámírez

Michel Cassir Segis Mat-

Thesis submitted to the Office of Graduate Studies in partial fulfillment of the requirements for the Degree of Doctor in Engineering Sciences.

Santiago de Chile, March, 2024

Dedico esta tesis a mi familia, por todo su apoyo incondicional y comprensión durante estos años. En especial a mi esposo, nuestras niñas, mi madre y mi hermana.

### ACKNOWLEDGEMENTS

The doctoral program was the most challenging proof in my life, not only in the academic file but also in terms of resilience and mental health. For this reason, it is important to name all the important people by my side during these years of training as a scientist.

I want to demonstrate my profound gratitude to my family for their love, kindness, understanding, and unconditional support throughout my entire life, specifically during these years of my doctoral thesis. In particular, I want to thank my mother and sister for their support and my husband for his infinite understanding.

Moreover, I am sincerely grateful to my advisors, Dr. Mamié Sancy and Dr. Carola Martinez, for their support, wisdom, and supervision over all these years of working together. It is important to mention other women scientists who inspire and support me, Dr. Carolina Guerra and Dr. Lisa Muñoz.

In addition, I thank my colleagues from the Laboratory of Electrochemical Materials for their companionship, understanding, and mutual support. Moreover, I want to thank the I2E laboratory (Interface, Electrochemistry & Energy) for their help and made my stay a wonderful experience.

Also, I want to thank my psychologist who played an essential role during this process, for all her dedication, patience, and advice.

Finally, I am deeply grateful to Pontificia Universidad Católica de Chile, in particular, to the "Vicerrectoria Académica de Investigacion" (VRI) for funding my doctoral studies and the Engineering Department of Mechanical and Metallurgic (DIMM UC) for supporting my research. Also, I would like to thank the Chilean National Agency of Research and Development (ANID), granted by Fondecyt grant N°11190500 and Millennium Institute on Green Ammonia as Energy Vector (MIGA) ICN2021\_023.

### **GENERAL CONTENT**

ACK	NOV	VLEDGEMENTS	iv
GEN	ERA	L CONTENT	v
TAB	LES	CONTENT	viii
FIGU	JRES	CONTENT	ix
RESU	JME	N	xi
ABS	TRA	СТ	xii
PRO	LOG	UE	xiii
DISC	CLAI	MER	xiv
I.	INT	RODUCTION	1
	1.1 1	Motivation	1
	1.2 \$	State-of-the-art	2
		1.2.1 General Background on Fuel Cells	2
		1.2.2 Molten Carbonate Full Cells	5
		1.2.3 Anodes in Molten Carbonate Fuel Cells	7
	1.3 1	Novel Aspects	10
II.	HYI	POTHESIS	11
	2.1 0	Objectives	11
		2.1.1 Main objective	11
		2.1.2 Specific objectives	11
III.	ME	ГНОDOLOGY	12
	3.1	Samples Fabrication	12
		3.1.1 Laser Powder Bed Fusion (LPBF)	12
		3.1.2 Spark Plasma Sintering (SPS)	12
		3.1.3 Heat Treatment	13
	3.2	Gravimetric measurements	14
	3.3	Electrochemical measurements	14
IV.	CHA	APTER I: Ni-Al Bronze in molten carbonate manufactured by LPB	F:
	effe	ct of porosity design on mechanical properties and oxidation	16
	4.1	Introduction	16
	4.2	Materials and Methods	17
		4.2.1 Sample Fabrication	17
		4.2.2 Morphological and Chemical Characterization	18
		4.2.3 Gravimetric Measurements	18

		4.2.4 Mechanical Characterization	19	
	4.3	4.3 Results and Discussion		
		4.3.1 Microstructural and Chemical Characterization	19	
		4.3.2 Mechanical Properties		
		4.3.3 Gravimetric Measurements		
	4.4	Conclusions		
V.	CHA	APTER II: The effect of adding CeO <sub>2</sub> nanoparticles to Cu-Ni-Al allo	oy for	
	high	temperatures applications		
	5.1	Introduction		
	5.2	Materials and Methods		
		5.2.1 Sample Obtention		
		5.2.2 Gravimetric Measurements		
		5.2.3 Morphological and Chemical Characterization		
		5.2.4 Mechanical Characterization		
		5.2.5 Electrochemical Measurements		
	5.3	Results and Discussion		
		5.3.1 Gravimetric Measurements		
		5.3.2 Microstructural and Chemical Characterization		
		5.3.3 Mechanical properties		
		5.3.4 Electrochemical measurements		
	5.4	Conclusions		
VI.	CHA	APTER III: Corrosion behavior of Ni-Al bronze by LPBF in n	olten	
	carb	onates		
	6.1	Introduction		
	6.2	Materials and Methods		
		6.2.1 Sample fabrication		
		6.2.2 Microstructure analysis		
		6.2.3 Surface analysis		
		6.2.4 Electrochemical measurements		
	6.3	Results and discussion		
		6.3.1 Microstructure characterization	45	
		6.3.2 Surface analysis		
		6.3.3 Electrochemical behavior		
		6.3.4 Microhardness	55	

	6.4	Concl	usions	55			
VII.	Chap	Chapter IV: Suitability of nickel aluminium bronze alloy fabricated by laser					
	powder bed fusion to be used in the marine environment						
	7.1	Introduction					
	7.2	Metho	odology	59			
		7.2.1	Sample fabrication	59			
		7.2.2	Sample characterization	50			
		7.2.3	Electrochemical measurements	50			
	7.3	.3 Results					
		7.3.1	Microstructure characterization	61			
		7.3.2	Electrochemical behaviour	62			
		7.3.3	Surface composition	65			
	7.4	Discu	ssion	67			
		7.4.1	Electrochemical analysis	67			
		7.4.2	Suitability of additive manufacturing to produce pieces with bett	er			
			corrosion performance	70			
	7.5	Concl	usions	72			
VIII.	GEN	JERAL	CONCLUSION	74			
REF	EREN	VCES		76			

### **TABLES CONTENT**

Table I-1: Materials and characteristics of hydrogen-oxygen fuel cells	. 4
Table IV-1: ID for NAB samples1	18
Table IV-2: Summary of compressive strain before and after exposure2	26
Table IV-3: Summary of surface alloy elements obtained using XPS2	29
Table V-1: Chemical composition of the Cu $-50$ Ni $-5$ Al + xCeO <sub>2</sub> (wt.%) alloys 3	32
Table VI-1: Metal alloys exposed to high temperatures	13
Table VII-1: Summary of the EIS parameters 7	70
Table VII-2: Comparison of electrochemical parameters 7	71

### **FIGURES CONTENT**

Figure I-1: Global change in electricity by source between 2019 to 2025	1
Figure I-2: Schematic representation of different fuel cell operations	3
Figure I-3: Schematic representation of fuel cell power application	4
Figure I-4: Schematic representation of molten carbonate fuel cells	6
Figure III-1: Schematic representation of Laser Powder Bed Fusion	. 12
Figure III-2: Schematic representation of Spark Plasma Sintering Process	. 13
Figure III-2: Schematic representation of each heat treatment.	. 13
Figure III-3: Schematic representation of the gravimetric measurements process	. 14
Figure III-4: Schematic representation of reference electrode	. 15
Figure V-5: Schematic representation of the gravimetric measurements	. 15
Figure IV-1: Micrographs of samples without and with thermal treatment	. 20
Figure IV2: FE-SEM images before and after exposure to molten salt	. 20
Figure IVI-3: EDS surface mapping before and after exposure t	. 21
Figure IV-5: GD-OES of bulk samples before and after exposure	. 22
Figure IV-6: XRD patterns of the bulk sample	. 24
Figure IV-7: Microhardness (HV) of the samples before exposure	. 24
Figure IV-8: Compression stress-strain curves of samples	. 25
Figure IV-9: The variation of weight and corrosion rate of samples	. 27
Figure IV-10: Physical model of the corrosion product evolution	. 28
Figure IV-11: XPS survey of sample before and after exposure	. 29
Figure V-1: Sample preparation and schematic representation	. 33
Figure V-2: The variation of weight of Cu-50Ni-5Al samples	. 35
Figure V-3: FE-SEM images before and after gravimetric measurements	. 36
Figure V-4: EDS surface mapping before and after	. 37
Figure V-5: XRD patterns of Cu-50Ni-5Al samples before and after	. 38
Figure V-6: Microhardness of the samples before exposure	. 39
Figure V-7: Open circuit potential variation of samples	. 40
Figure V-8: Nyquist diagrams of samples	. 40
Figure V-9: Effect of correction of electrolyte resistance on Bode plots	. 41
Figure VI-1: Micrograph of Ni-5Al and NAB alloys before exposure	. 46
Figure VI-2: FE-SEM and EDS analysis of Ni-5Al and NAB samples	. 47
Figure VI-3: XPS spectra of Ni-5Al and NAB alloys after exposure	. 48
Figure VI-4: Open circuit potential of Ni-5Al, NAB samples	. 49

Figure VI-5: Nyquist diagrams of Ni-5Al and NAB samples	. 50
Figure VI-6: Nyquist diagrams of Ni5Al and NAB samples	. 50
Figure VI-7: Bode plots of Ni-5Al and NAB samples	. 52
Figure VII-1: Radar chart used to compare different alloys	. 58
Figure VII-2: Schematic representation of each heat treatment	. 60
Figure VII-3: FESEM micrograph before and after exposure	. 61
Figure VII-4: XRD pattern for samples before exposure	. 62
Figure VII-5: Open circuit potential (E <sub>OC</sub> ) result	. 63
Figure VII-6: Nyquist plot and Bode diagrams after exposure	. 64
Figure VII-7: (a) LSV curve of NAB alloy after 30 days of exposure	. 65
Figure VII-8: XPS spectra of all samples before and after exposure	. 66
Figure V-9: The relative quantity of elements processed from XPS	. 66
Figure VII-10: Nyquist plot of samples after 30 days of exposure	. 68
Figure VII-11: Schematic representation of the oxide evolution a	. 69

#### RESUMEN

El crecimiento explosivo de la población global estas últimas décadas ha aumento del requerimiento energético, por lo que es necesario desarrollar nuevas tecnologías que sean más eficientes con respecto a las energías convencionales pero que además permitan reducir las emisiones de gases de efecto invernadero. En este contexto, las celdas combustibles representan a una de las tecnologías prometedoras que incluso pueden actuar como dispositivo de almacenaje o también como un sistema de respaldo para evitar problemas de intermitencias en sistemas eólicos o solares. Las celdas combustibles corresponden a un dispositivo electroquímico que convierte la energía química de un combustible directamente en energía eléctrica. Sus componentes son los electrodos (ánodo y cátodo), que son conductores de electricidad y el electrolito que es conductor iónico. En particular, las celdas de carbonato fundido (MCFC) utilizan hidrógeno como combustible y carbonatos fundidos como electrolito, las que alcanzan mayores potencias que la gran mayoría de las celdas combustibles, operando a temperaturas cercanas a 650 °C. Por lo que, a largo plazo, la corrosión de los electrodos y materiales usados en estos sistemas podría disminuir la vida útil de los componentes debido a las elevadas temperaturas de operación.

En esta tesis se planteó como objetivo general estudiar la microestructura y el comportamiento electroquímico de las nuevas aleaciones Cu-Ni-Al para ser empleada en celdas combustibles de carbonato fundido. Las aleaciones metálicas se fabricaron mediante metalurgia de polvos, tal como prensado en caliente y manufactura aditiva. La micro-macroestructura de las muestras se estudió antes y después de la exposición a los carbonatos fundidos (Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>) a 550 °C a través de microscopía óptica, microscopía electrónica de barrido de emisión de campo y difracción de rayos X. Además, se realizaron mediciones gravimétricas y espectroscopia de impedancia electroquímica en potencial de circuito abierto para analizar la corrosión de los electrodos en ambiente aireado y controlado.

Palabras claves: Celda combustible; carbonatos fundidos; ánodo; aleaciones de Ni; aleaciones de bronce al níquel y aluminio; Cu–Ni–Al; manufactura aditiva; metalurgia de polvos; corrosión; impedancia electroquímica; micro-dureza.

#### ABSTRACT

Global population growth has influenced further technological and scientific challenges, where the exponential increase in electricity demand stands out. In this context, it is necessary to continue researching alternatives to conventional energy generation to reduce greenhouse emissions. Fuel Cell technology is promising for lowering and storing carbon dioxide emissions in this context. It is a backup system to avoid intermittent problems with wind, solar, or other technologies. Fuel cells correspond to an electrochemical device that converts the chemical energy of a fuel directly into electrical energy. Their main components are the electrodes (anode and cathode), electronically conductive, and electrolyte. In particular, molten carbonate fuel cells use hydrogen as fuel, highlighting their excellent power. However, the high working temperature, close to 650 °C, is a disadvantage due to the reduction of the component's lifetime. Therefore, for a long-term operation, electrode corrosion behavior must be considered.

This thesis aims to study Cu-Ni-Al alloys' microstructure and electrochemical behavior for molten carbonate fuel cells. The metal samples were manufactured using powder metallurgical techniques, such as hot pressing and additive manufacturing. The porosity was analyzed using the Archimedes method. The micro-macrostructure of the samples will be studied before and after exposure to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> at 550 °C using surface analysis, such as optical microscopy, field emission scanning electron microscopy, and X-ray diffraction. Moreover, gravimetric measurements before and after exposure and electrochemical impedance spectroscopy at open circuit potential were used to analyze the corrosion of the anodes in an aerated and controlled environment.

Keywords: Fuel Cell, molten carbonates, anode, Ni-based alloy, nickel-aluminum bronze alloy, Cu–Ni–Al alloy, additive manufacturing, hot pressing, corrosion, electrochemical impedance, microhardness.

### PROLOGUE

Global population growth has influenced further technological and scientific challenges, where the exponential increase in energy demands stands out. Alternatives to conventional energy generation that produce no greenhouse gas emissions from fossil fuels reduce air pollution and avoid increasing global temperatures, which are some challenges that could be achieved using specific sustainable energies from renewable resources. In this context, fuel cell technology represents a technology that effectively reduces carbon dioxide emissions, which allows energy storage, works as a backup system to avoid intermittent problems, and can be used as a carbon dioxide ( $CO_2$ ) capture system.

Fuel cells (FC) correspond to an electrochemical device that converts the chemical energy of a fuel into electrical energy. Their main components are anode and cathode, electronic conductive materials with a sizeable electroactive surface area. In addition, electrolytes are a component of FC with high ionic and no electronic conductivity. Solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) are often used for their high efficiency. However, one of the disadvantages of this type of cell is the high working temperature, close to 800 and 600 °C, respectively, which consequently decreases the component's lifetime. Recent investigations have mainly focused on researching new electrodes with better corrosion resistance and mechanical properties because it is better if both technologies are separated. For the long-term operation of the cell, it is necessary to consider the electrode's structural stability and corrosion.

In this doctoral thesis, Cu-Ni-Al alloys were studied for MCFC applications using morphological, microstructural, mechanical, and electrochemical analysis. The effect of adding Cu and cerium oxide nanoparticles (CeO<sub>2</sub>-NPs) to Ni-Al anodes, which were manufactured using different powder metallurgy processes, was also analyzed.

This manuscript presents an introduction and state-of-the-art information related to the problem associated with electrodes and materials used in MCFC. In this doctoral thesis, three articles were published in WoS journals, and a fourth article is in preparation, which will be submitted soon in a WoS Journal. The scientific articles appear in a chapter for each one in this manuscript. **Article I** shows the mechanical properties and oxidation response of bulk and porous Ni-Al Bronze alloy manufactured by additive manufactured, laser powder bed fusion (LPBF), under molten carbonates in aerated condition. This article was published in the Materials Journal. **Article II** studies the effect of adding CeO<sub>2</sub> nanoparticles to Cu-Ni-Al alloy for high-temperature applications, comparing the mechanical and electrochemical properties. This article was published in the Nanomaterials Journal. **Article III** describes the electrochemical behavior of the Ni-Al alloy and Ni-Al Bronze alloy after exposure to molten carbonate at high temperatures under a controlled atmosphere. This article was submitted to the Corrosion Science Journal. **Article IV**, submitted in the Corrosion Science Journal, compares the Ni-Al and Ni-Al Bronze's corrosion behavior in marine media at room temperature.

### DISCLAIMER

This doctoral thesis is documented by the scientific articles listed below. These articles are included in the thesis text as chapters.

Article I <u>*C. Arcos*</u>, C. Guerra, J.A. Ramos-Grez, and M. Sancy\*.

"Ni-Al Bronze in Molten Carbonate Manufactured by LPBF: Effect of Porosity Design on Mechanical Properties and Oxidation."

Materials 16 (10), 3893. DOI: 10.3390/ma16103893 [2023]

WoS Journal | Second Quartile (Q2) | Impact Factor (2022): 3.4

Article II C.Martínez\*, <u>C. Arcos\*</u>, F. Briones, I. Machado, M. Sancy, and M. Bustamante.

"The effect of adding CeO<sub>2</sub> Nanoparticles to Cu-Ni-Al alloy for high temperatures applications".

Nanomaterials 14(2), 143. DOI: https://doi.org/10.3390/nano14020143 [2024] WoS Journal | First Quartile (Q1) | Impact Factor (2022): 5.3

Article III <u>*C. Arcos\**</u>, C. Guerra, M. Sancy\*, A. Ringuedé, C. Noël, V. Díaz, and M. Flores.

"Corrosion behavior of Ni-Al bronze by LPBF in molten carbonates."

Corrosion Science (submitted)

WoS Journal | First Quartile (Q1) | Impact Factor (2022): 8.3

Article IV <u>*C. Arcos*</u>, J.A. Ramos-Grez, M. Sancy, I La Fé-Perdomo, R. Setchi, and C. Guerra\*, "Suitability of nickel aluminum bronze alloy fabricated by laser powder bed fusion to be used in the marine environment."

*Corrosion science* 226, 111656. https://doi.org/10.1016/j.corsci.2023.111656 [2024] WoS Journal | First Quartile (Q1) | Impact Factor (2022): 8.3

### I. INTRODUCTION

#### **1.1 Motivation**

Global energy demand has increased significantly due to world population growth and the industrialization of developing economies [1,2]. Its production has been based mainly on fossil-fuel energy [2,3], increasing the global warming effect upon the rise of greenhouse gases in the atmosphere, such as carbon dioxide (CO<sub>2</sub>) [3]. Moreover, according to the last report in 2023 of the Intergovernmental Panel on Climate Change (IPCC), the "Sixth Assessment Report" reported that the world temperature is 1.1 °C warmer due to the greenhouse gas emissions from human activities, which undermines people's health, food security, water supply, and this consequence affects nature and people around the world [4]. In this context, the International Energy Agency (IEA) reported "A Global Pathway to Keep the 1.5 °C Goal in Reach", determinate that to ensure a liveable and sustainable future, it is necessary to deep, fast, and sustained reductions in greenhouse-gas emissions [5].

The total world renewable energy capacity was 1945 GW in 2021, 16% higher than the previous year. This capacity is divided into the following technologies: wind 845 GW, photovoltaics 942 GW, concentrated solar power 6 GW, biomass 143 GW, and geothermal power 14.5 GW [6]. Figure I-1 shows the growth of renewable energy as a function of time, revealing that renewable sources can overcome fossil fuels to generate electricity.



Figure I-1: Global change in electricity generation by source between 2019 to 2025 [7].

Chile is considered a specific country with a massive potential for renewable energy resources (RES) [8]. The Ministry of Energy promulgated a Decarbonization Plan for the electricity matrix in 2019, closing eight thermoelectric plants by 2024 [9]. An alternative energy source for fossil fuel is hydrogen (H<sub>2</sub>), which provides energy security and better pricing [10,11]. Therefore, H<sub>2</sub> can be produced through renewable resources (green

hydrogen), such as solar, wind, or geothermal [11], which provide clean electricity to the water electrolyser.

Furthermore, the energy efficiency of  $H_2$  increases (120 kJ/g) [12], with a calorific value three times higher than diesel oil (44 kJ/g) [13].

In Chile, the National Green Hydrogen Strategy (H2V) was promulgated in 2020 to stimulate and promote domestic applications and export H<sub>2</sub> from renewable energies. On the other hand, a further scientific-technological challenge is related to H<sub>2</sub> storage and energy conversion devices [14]. Consequently, it is necessary to study and develop technologies, such as fuel cells (FC), that generate energy by using H<sub>2</sub> without emitting polluting gases into the atmosphere because FC offers promising solutions to reduce the environmental impact of energy production by the possibility of generating electricity without emitting harmful substances into the atmosphere. All the technologies compromise as main components the electrolyte [15]. Moreover, it is essential to highlight that lithium carbonate is a vital electrolyte due to its high electrical conductivity [16]. This material has been promoted in the national lithium strategy in Chile since it considers its promotion in the refining processes and obtaining of lithium chemicals, such as carbonates (Li<sub>2</sub>CO<sub>3</sub>) and lithium hydroxide (LiOH) [17]. This is because Chile has one of the leading lithium reserves in the world in the Salar de Atacama.

### 1.2 State-of-the-art

### **1.2.1 General Background on Fuel Cells**

William R. Grove developed the first Fuel Cell (FC) concept in 1839, describing a clean form of combustion through the direct oxidation of carbon in an electrochemical device [18]. Fuel Cells are electrochemical devices that transform energy from electrochemical reactions into electrical and thermal energy, which can be used in transportation and portable or stationary applications [18]. Nowadays, it is agreed that FC technology represents an excellent opportunity for reducing the dependence on fossil fuels and carbon footprint production [19]. FC produces clean energy with a high conversion efficiency and system configuration that, in some cases, facilitates the easy capture of CO<sub>2</sub> [20,21]. Wang et al. [22] reported that FC corresponds to an electrochemical device that converts chemical energy directly into electrical energy; there are different kinds of fuel cells, as shown in Figure I-2, which can be classified according to the range of operation temperature. For example, low-temperature fuel cells between 20 °C and 200 °C, the phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), and polymer carbonate fuel cells (PEMFC). On the other hand, high temperatures are between 650 °C to 850 °C, the solid oxide fuel cell (SOFC) and molten carbonates fuel cell (MCFC).

The main components are electronically conductive materials (electrodes) with a sizeable electroactive surface area and an electrolyte with high ionic conductivity, as described by Mitsushima et al. [23]. In the FC, the anode is the negative electrode of the cell, where

the fuel (i.e., H<sub>2</sub>) is oxidized while the electrons are released. The cathode is the positive electrode in the system, where the oxidant (i.e., oxygen) is reduced and reacts with the cations, forming the final chemical product (i.e., water). The authors emphasized that electrolyte separates the anode from the cathode to avoid direct chemical reactions and electronic contact. It must be ionically conductive to enable an electrochemical reaction.



Figure I-2: Schematic representation of different fuel cell operations (adapted from references [23-25]).

The FC are classified according to the operation temperature, the chemical nature of the electrolyte, and the fuel type, as described by Da Rosa and Ordóñez [26]. Table I-1 shows the classification and characteristics of FC according to the working electrode. For example, Solid Oxide Fuel Cells (SOFC) and Molten carbonate fuel Cells (MCFC) are the most rapidly developing high-temperature fuel cell technologies [27]. The most used fuel corresponds to  $H_2$ , which is oxidized into the water at the anode, releasing electrons. Those electrons are involved in the oxygen ( $O_2$ ) reduction reaction at the cathodic side, forming carbonate ions ( $CO_3^{2-}$ ) in MCFC and oxide ions in SOFC. Then, the formed anions cross the electrolyte by migration and diffusion to help the oxidation at the anode.

The cathode and anode are porous materials that allow the transport of reactants and the removal of products, offering a sizeable geometric surface area or density of active sites for chemical reactions. Therefore, their microstructure and chemical composition must ensure mass transport and physico-chemical phenomena [26,27]. In this sense, the cathode and anodes should keep their high electrical conductivity and stability at elevated temperatures in the electrolyte environment. For FC, Nickel is commonly used to manufacture electrodes, such as anodes and cathodes. Several pilot power plants and commercial units have demonstrated the attractiveness of this technology. Nevertheless, its maturity is only apparent because it is necessary to reduce costs and extend the

durability of the material frequently used in this area. Table I-1 shows each fuel cell's electrodes' materials, fuel, and operation temperature.

Fuel Cell	Fuel	Anode	Electrolyte	Ion transfer	Cathode	Oxidant	Work temperature (°C)
SOFC: Solid oxide fuel cell	H <sub>2</sub> ,CO, CH <sub>4</sub>	Ni, ZrO <sub>2</sub>	Y <sub>2</sub> O <sub>2</sub> . ZrO <sub>2</sub> (ceramic)	O <sup>2-</sup>	Ni	O <sub>2</sub> (air)	850
MCFC: Molten carbonate fuel cell	H <sub>2</sub> ,CO, CH <sub>4</sub>	Ni- based	Li <sub>2</sub> CO <sub>3</sub> - K <sub>2</sub> CO <sub>3</sub> (molten carbonates)	CO3 <sup>2-</sup>	NiO	CO <sub>2</sub> +O <sub>2</sub> (air)	650
PAFC: Phosphoric acid	H <sub>2</sub> ,CO, CH <sub>4</sub>	Pt, Ru, C	H <sub>3</sub> PO <sub>4</sub> (phosphoric acid)	$\mathrm{H}^{\scriptscriptstyle +}$	Pt, C	O <sub>2</sub> (air)	200
PEMFC: Polymer electrolyte	H2, CH3OH	Pt, Ru, C	Cation exchange membrane	$\mathrm{H}^{+}$	Pt, C	O <sub>2</sub> (air)	80
AFC: Alkaline	$H_2$	Ni,Pt,Ru	KOH <sub>aq</sub> (alkalie salt solution)	OH-	Ag,Ni	$O_2$	100

Table I-1: Materials and characteristics of hydrogen-oxygen fuel cells [23,24].

Moreover, another critical parameter that classifies the FC technology is the power application range, classified as low, high, and very high-power generation [25], as shown in Figure I-3. First, low-power FC between 1W and 100W could be used in portable technologies such as phones, computers, or electronic equipment [28]. High-power FC is considered 1kW to 100kW and can be employed in transport systems, such as trains [29]. Finally, very high-power FC ranges between 1MW and 10MW for stationary applications as power generators [25]. Figure I-3 shows a schematic representation of fuel cell power application, according to the kind of Fuel Cell and power range.



Figure I-3: Schematic representation of fuel cell power application (adapted from references [25]).

Therefore, it is possible to observe that the fuel cells that present more power generation are the technologies that operate at high temperatures, such as SOFC and MCFC. Both fuel cells present different kinds of advantages. However, MCFC is highlighted because

it operates in lower temperatures than SOFC, close to 650°C. This is why it is considered an attractive option to develop medium-scale stationary units that generate between 100kW and 10MW [30]. These temperature conditions allow the distribution of the heat generated as a product from the fuel cell or combined heat and power [31]. It can also be used as CO2 separation in other industries, such as conventional power plants [31].

In the same way, this technology was studied for  $CO_2$  capture and storage devices (CCS). M.A. Abdelkareem et al. [31] proposed that MCFC is considered a promising method of CCS technology due to its possible integration with power plants. This fuel cell requires  $CO_2$ , which could complement industries that release  $CO_2$  into the atmosphere.

### **1.2.2 Molten Carbonate Full Cells**

Molten carbonate technology was developed in the 1950s [32]. The high operating temperature allows the use of different kinds of fuel, such as hydrogen, methane, biogas, and carbon monoxide. It also permits the application of non-noble material in the electrodes [33].

MCFC has been commercialized for stationary applications for over three decades of research and development [15]. It can be used in large-scale power generation due to its high capacity related to its single units. MCFCs were developed mainly in the USA, Germany, Italy, South Korea, and Japan [34–36]. The primary developer of this kind of fuel cell was Fuel Cell Energy Corporation, a company in the United States that developed carbonate fuel cells from 10 kW to 2 MW of electrical output, followed by the implementation of three commercial power plants from 300 kW to 2.8 MW [37-39]. The maximum effective area of a single cell may reach  $1 \text{ m}^2$ , the current density is around 120 mA/cm<sup>2</sup>, and the power generation efficiency is around 50%. In 1993, Hitachi and IHI in Japan developed carbonate fuel cells for stationary power, with a 1 MW power station composed of four fuel cell modules of 250 kW each unit [40-42]. Lu et al. [43] and POSCO [42], a South Korean company, described that an MCFC power station of 58.8 MW was composed of 21 fuel cell modules, which produced 2.8 MW each module, which provided power for 140,000 households. Wang et al. [22] reported that the operating temperature of MCFC is around 650 °C which is lower compared to SOFC. Meanwhile, the energy conversion efficiency of fuel-to-electricity is maintained near 47%, as described by Hacker et al. [23], Lu et al. [43], and Moreno et al. [44].

As mentioned above, in the MCFC, the anode and cathode are separated by the electrolyte that corresponds to a porous ceramic matrix [22] based on lithium aluminate (LiAlO<sub>2</sub>), as reported by Abdollahipour and Sayyaad [38]. A porous Ni alloy has been used as an anode for MCFC [22,38]. Nickel oxide has also been used as the cathode, allowing it to work at 1-10 atm of pressure. In this case, the fuel is supplied at the inlet of the anode side (H<sub>2</sub>, water, unconsumed methane, CO<sub>2</sub>, and carbon monoxide), and in the cathode, the O<sub>2</sub> and CO<sub>2</sub> are injected. Hence, a charge transfer process controls the electrochemical reaction of MCFC in a slow reaction system and a mass transfer process in a rapid reaction system, as reported by Lee [45]. Therefore, to produce the interchange of charges between the

anode and the cathode, the electrodes must be porous to allow the reacting gases to reach the interface electrode-electrolyte. The electrode reactions involved in the circuit are the following:

Anode: 
$$2H_{2(g)} + 2CO_3^{2-} \rightarrow 2H_2O_{(g)} + 2CO_{2(g)} + 4e^-$$
 (I.1)

Cathode: 
$$O_{2(q)} + 2CO_{2(q)} + 4e^- \rightarrow 2CO_3^{2-}$$
 (I.2)

Overall react.: 
$$2H_{2(g)} + O_{2(g)} + 2CO_{2(g)} \rightarrow 2H_2O_{(g)} + 2CO_{2(g)} + Electricity + Heat$$
 (I.3)

In the MCFC, chemical energy is related to the electrochemical reactions between the fuel,  $H_2$ , and oxidants,  $O_2$ , and  $CO_2$ , which place at on anode and cathode, allowing electrical energy generation. Therefore, the cathode catalyzes the reaction between  $O_2$  and  $CO_2$  towards the formation of  $CO_3^{2-}$  ions, as shown below:

$$O_{2(g)} + 2CO_{2(g)} + 4e^{-} \to 2CO_{3}^{2-} \tag{I.4}$$

The  $CO_3^{2-}$  ions migrate through the molten electrolyte to the anode, where the fuel is oxidized,  $H_2$ , and electrons are released, as can be seen below [23,27,46]:

$$2H_{2(g)} + 2CO_3^{2-} \to 2CO_{2(g)} + 2H_2O + 2e^- \tag{I.5}$$

The oxygen reduction reaction is the rate-determining step, often considered more complex and slower than the anode reaction [23,27,47–49]. Complementary mechanisms related to forming the  $CO_3^{2-}$  ions at the boundary between the electrolyte melt and gases were proposed that can involve the transport of species in the electrolyte through an oxo-Grotthuss mechanism via pyrocarbonate ions ( $C_2O_5^{2-}$ ) [50]. Figure I-.4 shows a schematic representation of a molten carbonate fuel cell adapted from the literature [51,52]. These systems can also be used as Carbon Capture and Storage (CCS) devices, with the second possibility of producing electricity.



Figure I-4: Schematic representation of molten carbonate fuel cells (adapted from references [51,52]).

The most common electrolytes used in MCFC are alkaline salt [53], for example, lithium and potassium carbonates (Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>), which have high ionic conductivity and good chemical stability [54]. However, the main problem is the cathode dissolution in the molten carbonate because it decreases the performance of the fuel cell [55]. On the other hand, nickel-based alloys are often employed in the cathode, even when they present oxidation and lithiation processes in situ in the molten carbonate. Therefore, the corrosiveness of molten carbonates is a significant difficulty leading to the cathode dissolution [55]. In this context, some authors, such as Meléndez-Ceballos et al. [56], Lee et al. [45], Ricca et al. [57], and Lair et al. [55] proposed to optimize the electrolyte used in MCFC, incorporating additives to avoid dissolution of the Ni from the cathode and to modify the cathode, employing different metallic coatings. Although MCFC technology has existed for decades, there are still challenges remaining to improve the efficiency of MCFC due to the high working temperature, which is a disadvantage and consequently decreases the system's lifetime. According to Hacker et al. [23] and Da Rosa and Ordóñez [26], for achieving a long-term operation of the FC, it is necessary to consider the following problems: reduction of the anode structural stability, cathode dissolution and corrosion caused by operating temperatures. For this reason, technological development is currently focused on researching new materials with good corrosion resistance and better structural properties when exposed to molten carbonates. Specifically, the material used as anode, since there is little research in this area.

### 1.2.3 Anodes in Molten Carbonate Fuel Cells

Nickel with small amounts of additives (Cr, Al) has been widely used as an anode material in MCFCs for the past two decades due to its good electrochemical activity and low polarization losses. However, MCFC operates at high temperatures, and creep and sintering problems of the anode produce a collapse of the anode, resulting in the electrolyte redistribution phenomenon due to a reduction in the contact between the anode and electrolyte matrix. However, the high operating temperatures imply that using precious metals is unnecessary for anodes. In this context, porous Nickel-Aluminum alloys (NiAl) are commonly used due to their low density, high melting point, excellent acid/alkali corrosion resistance, good oxidation resistance at elevated temperatures, and reasonable charge transfer conductivity.

Accardo et al. [58,59], Frattini et al. [60], and Youn et al. [61] analyzed the catalytic activity and mechanical strength of the electrodes. However, only some works have investigated the effect of the microstructure of the anode on the performance of FC. It should be mentioned that the standard porosity of MCFC anodes varies usually between 50-65%, while the pore size is around 2-3  $\mu$ m [46,59]. Wejrzanowski et al. [62] proposed that the material microstructure influences a porous electrode's catalytic performance and efficiency, reporting that the open pores offer a large geometric area for chemical reactions. Lee et al. [63] reported porosity and the average size of the pores due to a more excellent specific surface can improve the catalytic performance of an electrode. Therefore, the pore size drastically determines the area between the anode and molten

electrolytes, as reported by Bie et al. [64]. Furthermore, some authors found that the stability decreased with the loss of the anode porosity during the MCFC operation [59,65].

The anode can be reinforced by adding a third alloying metal to a binary Ni-based alloy or a hard metal oxide as a coating to the anode, blocking the dislocation movement and sintering that can occur during the cell operation [60,61,66–71]. The first strategy involves producing ternary alloys requiring heavy metallurgical or ball-milling processes. These ternary systems have interesting electrochemical properties, good ductility and stiffness, low creep resistance, and limited corrosion resistance. Therefore, more studies should assess reliable advantages and effective fabrication processes [46,58–61,63,66–68,70–75].

Consequently, to improve the structural stability, the incorporation of other metals into the initial alloy, such as titanium [60], chromium [61,67,76], and copper [68,76], among others, have been studied. Also, the incorporation of nanoparticles in commercial alloys such as zirconia oxides (ZrO<sub>2</sub>) [58,59] and cerium oxides (CeO<sub>2</sub>) [58] has improved the mechanical and electrochemical behavior of the anode.

### 1.2.3.1 Ternary alloy as electrode

Nguyen et al. [67] incorporated chromium into the NiAl anode, finding the best creep strain with Ni-5wt.%Al-10wt.%Cr. However, including this third alloying element did not improve the electrochemical performance. Kim et al. [66] analyzed the creep behavior of Ni-(4-7 wt.%)Ni<sub>3</sub>Al and Ni-5 wt.%Ni<sub>3</sub>Al-5 wt.% Cr anodes for molten carbonate fuel cells, reporting that the creep deformation decreased synergistically with the Ni3Al and Cr inclusion. Wee et al. [66] studied the impact of aluminum and chromium on the reference Ni-Al anodes, particularly for the creep and sintering resistance. The authors found that adding 5 wt.% Ni<sub>3</sub>Al and 3 wt.% Al obtained the most resistant material against the sintering, keeping the porosity close to 60% even at 1000 °C. Ni-Al alloys, including Ni3Al in the anode, show crack growth via the step-wise cracking mechanism under stress at 500-760 °C. Also, the researchers determined that the creep of anode for MCFC mainly occurred within 60 h from the start of operation. Li et al. [68] investigated Cu-35Ni-15Al as cast and porous materials, reporting that both had a Cu-rich phase, a Ni-rich phase, and intermetallics. Besides, the authors noted that the yield strength of porous alloys increased with the decrease in porosity and that the relationship between porosity and yield stress follows the Gibson-Ashby equation. Moreover, they determined that reducing the deformation temperature increased the yield strength for cast and porous alloy.

Incorporating copper (Cu) into the Ni-Al alloy can be an excellent opportunity to increase the thermal conductivity and mechanical resistance over a wide range of temperatures, making it an ideal material to work under extreme heat flow and compression conditions [68,77]. According to Klassert and Tikana [78], copper alloys are an important metallic material due to their metallurgical, physical, and chemical properties. For example, at high temperatures CuNi alloys show great tensile strength, also have good corrosion resistance. Other authors as Martínez et al. [79] study Cu and Ni separately and Cu-Ni

alloy and indicates that Ni presents the maximum strength, however Cu-Ni alloy presents intermediate values between pure Cu and Ni. It is essential to mention that the incorporation of metal can stabilize solid solution alloy, which means atoms of solvent metal are randomly replaced from their lattice position by atoms of solute metal, creating metallic bonds [80,81].

Also, Cu has good electrical conductivity and sintering properties. Cu-Ni-Al porous alloy can be an ideal material for MCFC anode [68,82]. Moreover, Fe could be introduced to the alloy Cu-Ni-Al, manufacturing a commercial Nickel-aluminum bronze or NAB alloy (Cu-Al-Ni-Fe) characterized by good corrosion behavior in hostile environments, such as marine environments [83]. Indeed, the corrosion behavior of alloys such as 51Fe-24Cr-20Ni and 5Fe-23Cr-58Ni-8Mo in molten salts has been investigated in the literature [84]. In this sense, Liu et al. [85] reported that adding ceria nanoparticles to a Cu-Ni anode improved the catalyst performance for the  $H_2$  oxidation reaction, which is critical to the electrode performance in MCFC. Accardo et al. [59,60] demonstrated that adding CeO<sub>2</sub>-NPs in Ni5Al alloy reduced the creep strain [58]. However, the investigations have not evaluated the influence of the CeO<sub>2</sub>-NPs on the micro-macrostructural and electrochemical behavior of the electrodes.

#### 1.2.3.2 Nanoparticles in Electrodes

The effect of nanoparticles on electrodes for FC has been investigated. For instance, Accardo et al. [59,60] found that the pore size decreased slightly when 1-5 wt. % of nanozirconia oxide (ZrO<sub>2</sub>-NPs) was added. The authors also reported that zirconia coated almost all the surfaces for a sample with 10 wt.% ZrO<sub>2</sub>-NPs, possibly due to the aggregation of the nanoparticles. While for samples with 3 wt. % ZrO<sub>2</sub>-NPs, the response was similar to the standard anode, reducing the creep strain [58,60]. On the other hand, a reduction of porosity and pore size was found for the Ni5Al sample with 3 wt. % ZrO<sub>2</sub>-NPs and nano-cerium oxide nanoparticles (CeO<sub>2</sub>-NPs), possibly due to the diameter of raw NiAl powders and the addition of many nanometric hard oxide particles [58]. The authors also found that nanoparticles reduced the creep strain. Accardo et al. [59] added nano-zirconia on NiAl anodes, reporting an enhancement in the physical, mechanical, microstructural, and electrochemical properties and long-term single-cell operations. Thus, the potential use of hard oxide nanoparticles is assessed to increase the performance of MCFC and anode properties.

Lee et al. [70] achieved better electrocatalytic activity and corrosion resistance using a  $Gd_2O_3$  electro-coated Ni-alloy. The authors obtained an open circuit potential of 1.015 V, maximum power densities close to 100-115 mW·cm<sup>-2</sup>, but no stable polarization curves when using carbon as fuel. Meléndez-Ceballos et al. [71,74,86] used CeO<sub>2</sub>, TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, and Nb<sub>2</sub>O<sub>5</sub> on the cathode, investigating the microstructural properties. Still, the authors did not use single-cell MCFC tests for electrochemical measurements in molten carbonate. Devianto et al. [74] analyzed the wettability and cell performance of a Ni anode coated by MgO and PbO for a direct-ethanol MCFC, obtaining low cell performances without analysis related to long-term durability.

### **1.3 Novel Aspects**

Ni-Al anodes are widely used for MCFC applications owing to their relatively low density, high melting temperature, excellent acid/alkali corrosion resistance, and good charge transfer conductivity. They are susceptible to creep and provoke sintering resistance, dramatically reducing fuel cell lifetime. In this context, generating efficient and stable anodes by incorporating alloying additives requires understanding the underlying mechanisms to engineer other efficient and stable anodes.

This work analyzed Cu-Ni-Al alloys as an anode for MCFC, studying the micro- and macrostructural properties and their corrosion. CeO<sub>2</sub>-NPs were added to the Cu-Ni-Al alloys to improve their performance as catalysts using electrochemical measurements.

### II. HYPOTHESIS

This work proposed the following hypothesis:

Hypothesis 1: Adding Cu to Ni-Al alloys enhances the corrosion properties in molten carbonate fuel cells. This is based on improving the passivity of the oxide film formed on Cu-Ni-Al.

Hypothesis 2: Adding CeO<sub>2</sub>-NPs to Cu-Ni-Al alloys increases the microhardness and improves the catalytic properties as an anode in molten carbonate fuel cells. This is based on reducing the grain size and increasing the active site.

### 2.1 Objectives

In this work, the following objectives are proposed:

### 2.1.1 Main objective

The main objective of this thesis is to study the effect of adding Cu and CeO<sub>2</sub>-NPs on the microstructural, morphological, and electrochemical behavior of the Ni-Al alloys in molten carbonate.

Based on the main objective, the following specific objectives are proposed:

### 2.1.2 Specific objectives

- Specific Objective 1: To analyze the physic-chemical properties of Cu-Ni-Al alloys.
- Specific Objective 2: To evaluate microstructural and mechanical properties of Cu-Ni-Al alloys.
- Specific Objective 3: To study the electrochemical behavior of Cu-Ni-Al alloys.

### III. METHODOLOGY

### 3.1 Samples Fabrication

### 3.1.1 Laser Powder Bed Fusion (LPBF)

The Cu-11Al-5Ni-4Fe (NAB) and Ni-5Al samples were manufactured using Laser Powder Bed Fusion (Chapters I, III, and IV). For the Ni-5Al sample, the powder size was smaller than 45  $\mu$ m, and for the NAB sample, the powder size was smaller than 40  $\mu$ m. The equipment utilized was GE-Concept Laser Mlab using a 200R machine, and the selective laser melting was set to 30  $\mu$ m and 80  $\mu$ m,180 W, and the laser speed was kept at 600 mm·s<sup>-1</sup>. The total volumetric energy density was 125 J·mm<sup>-3</sup>. The Cu-11Al-5Ni-4Fe sample was fabricated over a copper platform and Ni-5Al alloy was manufactured on a 100 x 100 mm stainless-steel platform. The samples were removed from the platform using wire electrical discharge machining at 100 V and 2.5 A.



Figure III-1: Schematic representation of Laser powder bed fusion (adapted from Reference [87]).

### 3.1.2 Spark Plasma Sintering (SPS)

Cu-50Ni-5Al (Chapter II) was manufactured using spark plasma sintering (SPS). Previously, the pure powders, Nickel <10  $\mu$ m, Copper <63  $\mu$ m, and Aluminum <60  $\mu$ m, were mixed using mechanical alloying in a Planetary mill PQ4 Across International, obtaining powder compositions of Cu-50Ni-5Al (wt.%). The milling conditions included a ball–a–powder ratio (BPR) of 10:1 and 2 wt.% stearic acid as a control agent under an inert Ar atmosphere. The milling time was 100 h effective, and there was an on/off cycle of 30/15 min at a speed of 350 r.p.m. Then, cerium oxide nanoparticles (CeO<sub>2</sub> - NPs) were added in 1, 3, and 5 wt.%, using a particle size smaller than 25 nm, performed in a Mixer Y–type Astecma for 1 h. Later, Cu–50Ni–5Al samples without and with CeO<sub>2</sub>–NPs were consolidated by SPS, using a Fuji Electronic Industrial SPS1050. The samples were heated from room temperature to 800 °C at a heating rate of 100 °C ·min<sup>-1</sup>, applying a pressure of 50 MPa simultaneously during the heating, keeping at the sintering temperature for 5 min. The entire SPS process was kept under a vacuum of approximately 20 Pa. Finally, the samples were cooled to room temperature at a cooling rate of roughly

10 °C  $\cdot$ s<sup>-1</sup> in the SPS chamber. Figure III-2 shows a schematic representation of the entire process.



Figure III-2: Schematic representation of Spark Plasma Sintering Process (adapted from Reference [88]).

### 3.1.3 Heat Treatment

The NAB and Ni5Al samples (Chapters I and IV) were thermally treated, applying a quenching and tempering process (Q+T). This thermal treatment consisted of heat treatment at 900 °C for 1 h, then a rapid cooling in water, heating to 700 °C for 5 h, and finally cooling in the air. Meanwhile, in the annealing process (A), the samples were heated to 900 °C for 2 h, followed by a cooling in the furnace [89,90]. Figure III-3 shows a schematic representation of the heat treatment processes.



Figure III-3: Schematic representation of each heat treatment "Q+T" and "A" is annealing (from Reference[91]).

### 3.2 Gravimetric measurements

To determine the mass variation and corrosion rate, all samples were exposed to  $Li_2CO_3$ - $K_2CO_3$  molten carbonate inside an alumina crucible at  $550 \pm 5^{\circ}C$  for 21 days in aerated conditions in a furnace. Every 7 days, samples were removed from the stove and cleaned to eliminate the crystallized salt form on the metal surface using beakers filled with 25 mL of hot distilled water (~100 °C), which were placed in a sonicator bath Elma D-78224 for 30 min. Subsequently, the samples were dried with hot air and weighed until they reached a constant value, as reported by the ASTM G1-03 [92]. Figure III-4 shows the gravimetric measurements carried out during this thesis.



Figure III-4: Schematic representation of the gravimetric measurements process.

### 3.3 Electrochemical measurements

The electrochemical measurements were performed using a potentiostat/galvanostat (Solartron Analytical Xm) and a three-electrode electrochemical cell under aerated and deaerated media. Ni-5Al, Cu-50Ni-5Al, and Cu-11Al-5Ni-4Fe alloys were used as working electrodes. A gold wire welded to a silver wire was employed as the counter electrode. A silver wire dipped into an Ag<sub>2</sub>SO<sub>4</sub> ( $10^{-1}$  mol·kg<sup>-1</sup>) saturated Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> contained in an alumina tube sealed by a porous alumina membrane (frit) was used as the reference electrode (Ag/Ag<sup>+</sup>) [93], as shown in Figure III-5.



Figure III-5: Schematic representation of reference electrode.

The electrochemical measurements under controlled media were done using a constant flow of  $H_2/N_2$  in a 40/10 ml·min<sup>-1</sup> ratio. The electrolyte was a molten carbonate (Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>) kept at 550 °C.

The open circuit potential and impedance data were collected during five days of exposure to molten carbonate. The electrochemical impedance spectroscopy (EIS) was measured in duplicates between 65 kHz and 3 mHz, using eight points per decade and an amplitude of 10 mV. EIS measurements were carried out at  $E = E_{OC}$  and  $E = E_{OC} \pm 30$  mV.



Figure III-6: Schematic representation of electrochemical set-up (adapted from Reference [94]).

### IV. CHAPTER I: Ni-AI BRONZE IN MOLTEN CARBONATE MANUFACTURED BY LPBF: EFFECT OF POROSITY DESIGN ON MECHANICAL PROPERTIES AND OXIDATION

### 4.1 Introduction

Global energy demand has increased significantly due to world population growth and the industrialization of developing economies [2]. Energy production has been based mainly on fossil-fuel energy [95], which has increased the global warming effect with the rise of greenhouse gases, such as carbon dioxide  $(CO_2)$ , in the atmosphere [64].

Fuel cell technology has been explored as an excellent alternative for reducing the dependence on fossil fuels and carbon footprint production because the fuel cells use clean energy with a high conversion efficiency, also allowing CO<sub>2</sub> capture [22,96]. Fuel cells are electrochemical devices that convert chemical energy [26]. Molten carbonate fuel cells (MCFCs) are one of the most rapidly developing hightemperature fuel cell technologies [22] that offer promising solutions to reduce the environmental impact of energy production by generating electricity without emitting harmful substances into the atmosphere. The main components are electrodes and an electrolyte membrane with high ionic conductivity [15]. The fuel frequently used is  $H_2$ , which is oxidized into the water at the anode, releasing electrons which are involved in the oxygen  $(0_2)$  reductio reaction at the cathodic side, forming carbonate ions  $(C0_2^{2-})$  in MCFCs. The electrolyte separates anode and the cathode, which corresponds to a porous ceramic matrix [22,64], such as a ceramic lithium aluminum oxide (LiAlO<sub>2</sub>), embedding a mixture of the molten carbonate, as reported by Abdollahipour and Sayyaad [38]. The cathode and anode are porous materials, offering a sizeable geometric surface area or density of active sites for chemical reactions [26,27]. Although MCFC technology has existed for decades, some open challenges remain for a real breakthrough regarding durability, lifetime, and cost of core components [15,26].

Ni has been widely used in MCFCs for the past two decades due to its good electrochemical activity and low polarization losses. However, high temperatures produce a collapse of the anode due to the creep and sintering problems, decreasing the contact between anode and electrolyte matrix. However, the high operating temperatures imply that using precious metals is unnecessary for anodes. Porous nickel-aluminum alloys (Ni-Al) are commonly used due to their low density, high melting point, excellent acid/alkali corrosion resistance, good oxidation resistance at elevated temperatures, and good charge transfer conductivity. The standard porosity of anodes varies between 50 and 65%, with a pore size of around  $2-3 \mu m$  [26,27]. Anodes are affected by compressive and thermal stresses during the operation of MCFCs, which favor the creep deformation that decreases their porosity and electrochemical activity [59,72]. Even though this alloy has been shown to be ideal as an anode, some authors found that the loss of porosity during the MCFC operation influences the catalytic performance and efficiency of anodes [58,59,73]. Some alloying elements have been incorporated into NiAl anodes to improve their structural stability, such as titanium [60], chromium [63,67], and copper [68,76]. Studies have demonstrated that the anodes can be mechanically reinforced by adding a third alloying

element to the NiAl or incorporating a hard metal oxide as a coating to block the dislocation movement and the sintering that can occur during the cell operation [60,82]. These ternary systems have interesting electrochemical properties, good ductility and stiffness, low creep resistance, and good corrosion resistance [56,60]. Nguyen et al. [67] incorporated chromium into the Ni-Al anode, finding the best creep strain with Ni-5wt.%Al-10wt.%Cr. However, the chromium addition did not improve the electrochemical performance. Kim et al. [75] analyzed the creep behavior of Ni-(4-7 wt.%)Ni<sub>3</sub>Al and Ni-5wt.%Ni<sub>3</sub>Al-5wt.%Cr anodes for MCFC, finding that the creep deformation decreased synergistically with the Ni<sub>3</sub>Al and Cr inclusion. Li et al. [68] investigated a Cu-Al anode as cast and porous materials, reporting a Cu-rich phase, a Nirich phase, and an intermetallic composed of both materials. In addition, the authors noted that the yield strength of porous alloys increased with decreased porosity and that the relationship between porosity and yield stress follows the Gibson-Ashby equation. Moreover, they determined that reducing the deformation temperature increased the yield strength for cast and porous alloys. Although Ni-Al anodes are widely used for MCFC applications, a loss of the anode porosity and corrosion in molten carbonate due to the high temperatures have been reported.

Adding copper (Cu) into Ni-Al alloy can reduce the cost of anode manufacturing, increasing thermal conductivity and mechanical resistance. Therefore, Cu-Ni-Al can be ideal for extreme conditions [68,77], such as an anode for MCFCs [68,82]. Moreover, Fe could be introduced to the alloy Cu-Ni-Al, manufacturing a commercial NAB (Cu-Al-Ni-Fe) alloy characterized by a good corrosion behavior in hostile environments, such as marine environments [83]. Indeed, some authors study the corrosion behavior of alloys such as 51Fe-24Cr-20Ni and 5Fe-23Cr-58Ni-8Mo in molten salts [84].

In this work, a new porous Cu-Al-Ni-Fe alloy was fabricated by laser powder bed fusion (LPBF) through selective laser melting (SLM), which allows for the fabrication of samples with different pore geometry at a laboratory scale [97]. This is unlike other techniques that use salts to generate arbitrary porosity, such as conventional powder metallurgy [98]. The samples were exposed to molten carbonate in an aerated medium to simulate the MCFC conditions to better understand the anode degradation during exposure, particularly its mechanical properties and corrosion resistance.

### 4.2 Materials and Methods

### **4.2.1 Sample Fabrication**

Cu-11Al-5Ni-4Fe wt.% alloyed powders (<40  $\mu$ m, CNPC powder group CO) were used to manufacture the anode samples through a selective laser melting (Concept Laser Mlab using 200R Ge machine, Boston, MA, USA) that was set to 30  $\mu$ m and 80  $\mu$ m for the layer thickness and hatch space. In contrast, the power and laser speed were kept at 180 W and 600 mm·s<sup>-1</sup>. Samples were fabricated with a cylindrical shape, constructed vertically over a copper platform with two lattice types with a length and diameter of 6 mm and 8 mm. After fabrication, samples were removed from the Cu platform using wire electrical discharge machining (W-EDM) at 100 V and 2.5 A. Table IV-1 shows the ID of samples and their characteristics.

Table IV-1: ID for NAB samples.							
ID	Lattice Type	Heat Treated	Image				
В	Bulk	No					
1G	0 1 1	No	STA WAR				
1GHT	Gyroid + wall	Yes					
2G	G 11	No	1210 1990				
2GHT	Gyroid	Yes	1950 Mars				

Before exposure, the metal samples were polished by wet grinding with grit sandpaper from #400 to #4000 to reveal their microstructure and then polished with colloidal silica suspension. Some samples were thermally treated at 900 °C for 2 h and then cooled in a furnace to analyze the effect of annealing on the mechanical and microstructural behavior.

### 4.2.2 Morphological and Chemical Characterization

The apparent porosity was estimated using Archimedes' method, based on the Standard Test ASTM C373-88 [99] and through image analysis using the open-source program ImageJ. The microstructure was revealed using 5 g of Fe<sub>3</sub>Cl, 10 mL of HCl, and 100 mL of distilled water for 10 s. Images were obtained using an optical microscope (OM), Olympus model GX41, and a field-emission scanning electron microscope (FE-SEM), QUANTA FEG 250 [100]. The surface analysis was analyzed using X-ray Photoelectron Spectroscopy (XPS), employing a K-alpha photoelectron spectrometer (Thermo Scientific). The alloy phases were characterized with X-ray diffraction (XRD) using Rigaku equipment, MiniFlex 600, detector D/tex Ultra 2 High-Speed 1D, and equipped with a Cu K $\alpha$ 1 radiation source ( $\lambda$  = 1.54056 Å). The chemical composition depth profiles of the corrosion products were measured using glow-discharge optical emission spectroscopy (GD-OES, Spectruma GDA 750 HR).

#### **4.2.3 Gravimetric Measurements**

Anode samples were exposed to  $Li_2CO_3$ -K<sub>2</sub>CO<sub>3</sub> molten salt at 550 °C for 21 days in aerated conditions, with eutectic composition (62:38 mol. %), as described by Cassir et al. [18], Ricca et al. [57], and Lair et al. [55]. Gravimetric measurements of samples were carried out in quadruplicates to ensure replicability. Every 7 days, samples were removed from the furnace and cleaned to eliminate the crystallized salt from the entire surface by using beakers filled with 25 mL of hot distilled water (~100 °C), which were placed in a sonicator bath (Elma D-78224 Singen/Htw, Singen, Germany) for 30 min for bulk samples and 1 h for porous samples. Subsequently, the samples were dried with hot air and weighed until they reached a constant value, as reported by the ASTM G1-03 [92]. The average mass (%) was calculated using Equation (IV.1).

$$\frac{\mathrm{m_{i}}-\mathrm{m_{f}}}{\mathrm{m_{i}}} \times 100 \qquad (\mathrm{IV.1})$$

where  $m_i$  and  $m_f$  are the initial and final sample masses at different exposure times. The corrosion rate (CR) was estimated following the ASTM G1-03 [92] using the following equation:

$$\frac{(K \times W)}{(A \times T \times D)} \tag{IV.2}$$

where K is a constant in the corrosion rate equation, T is the time of exposure in hours, A is the area in centimeters square (cm<sup>2</sup>), W is the mass loss in grams (g), and D is the density in grams per cubic centimeters (g·cm<sup>-3</sup>).

#### 4.2.4 Mechanical Characterization

Before exposure, the microhardness of samples was evaluated using a micro-Vickers durometer in triplicate (Wilson<sup>®</sup> VH1150 Macro Vickers Hardness Tester, Ontario, Canada) under 0.5 kgf of force, and the compression test was assessed following the ASTM E9 using an Instron 4200 machine with a speed test of 0.05 min<sup>-1</sup>.

#### 4.3 **Results and Discussion**

#### 4.3.1 Microstructural and Chemical Characterization

In this work, the apparent porosity and density of bulk (B) and porous samples (G) in asbuilt conditions were evaluated, determining a porosity near  $3.5 \pm 1.7\%$  for the B sample,  $81.4 \pm 12\%$  for the 1G sample, and  $84.9 \pm 11\%$  for the 2G sample and a density close to 7.3 g·cm<sup>-3</sup> for the B sample, 1.36 g·cm<sup>-3</sup> for the 1G sample, and 1.15 g·cm<sup>-3</sup> for the 2G sample.

Figure IV-1 shows the micrographs of the B and G samples in as-built conditions, revealing a martensite phase with an acicular shape, as shown in Figure IV-1a–c [101]. After the heat treatment, a spheroid structure was formed on the 1GHT and 2GHT samples, as described in annealing steels [102]. Therefore, it is possible to appreciate that after the heat treatment, the martensite disappears, and it is only possible to observe the grain form with a spheroid structure. Figure IV-1 reveals that the B, 1G, and 2G samples exhibit a microstructure composed of a darker matrix and precipitated phases in a lighter color [103,104], identifying the martensitic phase as  $\beta'$ , also known as "retained  $\beta$ " or as  $\beta'$  phase [105]. The heat treatment influenced a microstructure change, as shown in Figure IV-1d,e. For example, the lighter zones were related to the  $\alpha$  phase, which is a copperrich solid solution [106], as reported by Tavares et al. [107], who stated that the heat treatment propitiated the  $\beta'$  transformation to the equilibrium one [108], which can be attributed to the darker regions.

Figure IV-2 shows the FE-SEM images that reveal that the bulk sample (B) had a homogeneous surface with some pores whose diameter was near  $2-5 \mu m$  (white arrow) formed possibly during fabrication, as shown in Figure IV-2a. In contrast, porous samples

had a more heterogenous surface, with some unmelted spheric powders, sticks, and fissures, as seen in Figure IV-2b–e. After exposure to molten salt at 550 °C, all samples had a heterogeneous surface with inlays (lighter zones) and sharp or ridged geometric shapes (highlighted with black arrows), which could be molten salt deposits and corrosion products on the surface, as reported by Gupta and Mao [109]. Some authors have described the formation of different oxides on the metal surface when exposed to molten salts with Li content, such as LiAlO<sub>2</sub> and LiFeO<sub>2</sub>, which can be formed due to the high reactivity of Al and Fe and reactive in oxidizing environments containing CO<sub>3</sub> [84,110–112], which can diffuse to the surface [84,111,112]. It has also been reported that CuO, Cu<sub>2</sub>O, and NiO have low solubility in molten salt [84,111,113] and, thus, can be adhered to the metallic surface.



Figure IV-1: Micrographs of (a) bulk, (b,d) gyroid with wall structure, and (c,e) gyroid structure. Samples (b,c) without and (d,e) with thermal treatment.



Figure IV-.2: FE-SEM images of (a,f) bulk, (b,d,g,i) gyroid with wall structure, and (c,e,h,j) gyroid structure (a–e) before and (f–j) after exposure to molten salt. Samples (a–c,f–h) without and (d,e,i,j) with thermal treatment.

Figure IV-3 shows the EDS elemental mapping performed on the sample surface, revealing that the metal surface was composed mainly of Cu and Al for porous samples, 1G and 2G, before exposure. The Al content increased after heat treatment in the 1GHT and 2GHT samples by an even more significant amount than Cu, which could be related to the more negative reduction potential of alumina oxide in comparison to copper oxides, forming a thin alumina (Al<sub>2</sub>O<sub>3</sub>) film over the surface, as described previously by Hasegawa et al. [114]. The Cu content was more remarkable than the Fe, Al, and Ni content post-exposure.

In addition, FE-SEM analysis revealed local zones rich in Cu and Fe content and a more homogeneous distribution of Ni and Al. Tang et al. [112] studied the corrosion resistance of a Ni-10Cu-11Fe alloy as an anode exposed to molten carbonate in the presence of oxygen, determining that the oxide formation was mainly composed of Fe and Cu. In addition, Spiegel et al. [115] reported the formation of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) on Fe-based alloys after exposure to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> eutectic mixture, followed by the appearance of LiFeO<sub>2</sub> or LiFe<sub>5</sub>O<sub>8</sub>, which are highly insoluble in the molten carbonate [116]. Audigié et al. [110] studied a nickel–aluminide coating exposed to a eutectic mixture of NaNO<sub>3</sub>-KNO<sub>3</sub> and observed the presence of NiAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> oxides. De Miguel et al. [84] established the existence of aluminum-lithium oxide (LiAlO<sub>2</sub>) on the surface of an alloy due to the high reactivity of aluminum in molten salts in aerated environments, which improved the corrosion resistance of the material [110].



Figure IVI-3: EDS surface mapping of (a,f) bulk, (b,d,g,i) gyroid with wall structure, and (c,e,h,j) gyroid structure, (a–e) before and (f–j) after exposure to molten salt. Samples (a–c,f–h) without and (d–e,i–j) with thermal treatment.

Figure IV-4 shows FE-SEM images and EDS analysis of a cross-section of bulk and porous samples after 21 days of exposure to the molten salt, revealing a homogenous distribution of the alloying elements on the alloy. For porous samples, a thin film was formed that was composed principally of Fe, then Al, followed by a Ni-rich zone, whose thickness was approximately 1.5  $\mu$ m, which depended on the porous design. The heat treatment did not drastically influence the layer formed on these samples. However, a local zone in Cu content was determined [112,116,117]. It has been proposed that at the beginning of the exposure to the molten salt, Cu, Al, Fe, and Ni are oxidized, generating the oxide layer. Tang et al. [112] exposed a Ni10Cu11Fe alloy to Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> salts. The authors found an inner oxide layer composed mainly of NiFe<sub>2</sub>O<sub>4</sub> that could be formed

by the reaction between  $Fe_2O_3$  and NiO, which is more stable than  $Fe_2O_3$ . In the NAB alloy, Fe is also the most reactive metal in the alloy [112] that can diffuse to the surface quickly. Therefore, an intermediate layer rich in Cu and Ni oxides (CuO, Cu<sub>2</sub>O, and NiO) can form. Goupil et al. [117] established that the Cu<sub>65</sub>Ni<sub>20</sub>Fe<sub>15</sub> alloy used as an inert anode for aluminum electrolysis in oxygen presence can induce the formation of Fe<sub>2</sub>O<sub>3</sub> precipitates and CuO, and then, Fe<sub>2</sub>O<sub>4</sub> can be formed. Luo et al. [116] indicated that after a short exposure time, the corrosion products formed on the sample SS316L surfaces are mainly LiFeO<sub>2</sub> with a small amount of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, and LiFe<sub>5</sub>O<sub>8</sub> and an inner layer of NiO. Moreover, a thin alumina film (Al<sub>2</sub>O<sub>3</sub>) could form on the surface samples [114]. Therefore, all this oxide forms a layer that achieves stability over time.





Figure IV-5 shows a compositional depth profile obtained using GD-OES of the bulk sample before and after exposure, revealing the variation of each element (O, Al, Fe, Ni, and Cu) across the sample. Up to a depth of 1.5  $\mu$ m, the oxygen had the highest mass concentration, which decreased drastically, which could be considered the oxide layer thickness. Cu was the second predominant element up to 1.5  $\mu$ m, which increases until it reaches a stable value. Al was the third element, up to approximately 2.1  $\mu$ m, reducing its content later. Fe, Al, and Ni have low quantities on the surface, which increased near 1.5  $\mu$ m, demonstrating the transition from an oxide composed mainly of copper until it arrived at the base metal. According to the GD-OES, the oxide was formed primarily by Cu. H, the inner layer, is composed of other alloying elements. In particular, the B sample before exposure had a more significant amount of Fe on the surface, later Al and Ni. After exposure, Ni content increases in the inner layer.



Figure IV-5: GD-OES of bulk samples (a) before and (b) after 21 days of exposure to molten salt. (--) O, (--) Al, (--) Fe, (--) Ni, and (--) Cu.
Figure IV-6 shows the XRD patterns of bulk samples in as-built conditions and after the heat treatment. The patterns show the presence of  $\alpha$ -Cu (FCC),  $\kappa$ -phases (intermetallic), and the metastable  $\beta'$ -phase (martensite) in both conditions. The pattern of bulk samples in as-built conditions demonstrated thicker peaks and less smoothness than after heat treatment, which was attributed to internal defects due to rapid solidification [101]. After heat treatment, a higher amount of crystalline phases was determined, which can correspond to the equilibrium phases, such as the  $\alpha$ -Cu that can reduce the residual stress and homogenizes the structure. Alkelae et al. [118] described the microstructure transition at different cooling rates for Cu-11Al-5Ni-4Fe (in wt.%), showing through a phase diagram that the  $\beta$ -phase (BCC) is stable at high temperatures (above 1050 °C). The cooling rate can favor the formation of intermetallic compounds, such as  $\kappa$ -phase, and solid solutions, such as  $\alpha$ -phase (FCC). Therefore, the B sample could have good mechanical properties because the  $\alpha$ -phase is a ductile and malleable phase that can reinforce the  $\kappa$ -phase. It is important to note that the martensite did not influence the XRD pattern after exposure because it is a metastable phase and decomposed in the stable phases at the test temperature.

### **4.3.2 Mechanical Properties**

Figure IV-7 shows the microhardness of bulk and porous samples measured on the surface of the samples. The bulk sample exhibited a maximum value of  $315.6 \pm 15.8$  HV, followed by the 2G sample with  $304.1 \pm 14.5$  HV and the 1G sample with  $279.7 \pm 18.9$  HV. After the heat treatment, the microhardness decreased by half, close to  $164.2 \pm 3.2$  HV for the 2GHT sample and around  $152.2 \pm 10.9$  HV for the 1GHT sample. According to Orzolek et al. [104], the microhardness decreases when the NAB alloy is heat-treated due to a microstructural transformation. For example, the martensitic microhardness is around 400 HV, while the  $\alpha$ -phase value is near 320 HV. Lv et al. [119] determined that the microhardness in a NAB alloy was about 280 HV, which decreased to 245 HV after heat treatment at 675 °C for 2 h, which can be associated with a transformation of  $\beta'$  phases into  $\alpha$ . The B, 1G, and 2G samples had higher hardness, close to 300 HV, which was reduced to near 160 HV for the 1GHT and 2GHT samples after the heat treatment. After exposure, the micro-hardness was not registered in this work due to the corrosion products and deposits formed on the surface that were not soluble in hot water.



Figure IV-6: XRD patterns of the bulk sample in as-built condition and after heat treatment (HT).



Figure IV-7: Microhardness (HV) of the samples before exposure.

Figure IV-8 shows compression stress–strain curves of samples before and after exposure to the molten salt. The B sample exhibited the highest compressive strength and elongation due to its lower porosity [120]. The 1G porous sample presented a greater strength than the 2G sample, which has a similar porosity, around 84%, which in this case had the shape of a gyroid lattice [120], which defines its mechanical properties. It has been shown that outer shell wall inclusion in highly porous structures reinforces the alloy, improving the maximum compressive strength, and is the factor that most impact the compressive mechanical properties [121].



Figure IV-8: Compression stress–strain curves of (a) bulk, (b,d) gyroid with wall structure, and (c,e) gyroid structure. Samples with "empty symbols" before and with "filled symbols" after 21 days of exposure to molten salt.

Before exposure, porous samples were drastically influenced by the thermal treatment, revealing that annealing decreases the maximum strength and increases the elongation due to the residual stress release accumulation during the manufacturing process [108]. After 21 days of exposure to molten salt, the material suffered a drop in its compressive mechanical properties, especially for samples without heat treatment, reaching a maximum strength similar to that of the heat-treated samples. The latter can be attributed to the prolonged exposure of samples to a 550 °C temperature, which modified their internal microstructure, fostering their similarities. Therefore, the maximum strength diminished in all samples, but the elongation increased, which can be related to grains coarsening [66] during the exposure, since the temperature provided enough energy to increase the grain size [108], according to the phase diagram [118]. Additionally, the post-processing of the samples is unnecessary if the alloy is exposed to high temperatures, and thus, it can be used in its as-built condition.

Wee et al. [66] reported the creep behavior for porous anodes in fuel, varying the load between 0.1 and 0.7 MPa and with different temperatures. The Ni-Cr and Ni-Al anodes revealed an adequate creep rate between 5 and 10% creep strain at 100 h. The bulk NAB alloy achieved a 0.01% creep rate after 1000 h using stress of 3.1 MPa at 550 °C [122], which is promising for its use as an alloy in MCFCs. Table IV-2 summarizes the effect of the heat treatment on the maximum strength and elongation of the NAB samples, as bulk and gyroid, extracted from the compressive strain curves. The porous samples decreased the maximum of stress in comparison to that of the bulk samples, which was more drastic after exposure. However, the elongation was not significantly influenced by the porosity and exposure.

Samula ID	Bef	ore Exposure	After Exposure				
Sample ID	$\sigma_{\rm UTS}$ (MPa)	Max. ε (%)	% var. *	$\sigma_{\rm UTS}$ (MPa)	Max. ε (%)	% var. *	
В	$1140.9\pm27.1$	$20.8\pm0.5$	100	1415.5	59.9	100	
1G	$317.7\pm10.0$	$19.0\pm0.5$	27.8	$177.4\pm6.5$	19.1	12.5	
2G	$138.1\pm6.0$	$19.5\pm5.9$	12.1	$50.6\pm5.7$	$24.6\pm4.9$	3.6	
1GHT	$237.7\pm5.6$	$37.3\pm0.2$	20.8	168.7	$29.2\pm5.3$	11.9	
2GHT	$96.8\pm33.0$	$51.8 \pm 10.4$	8.5	$64.9 \pm 10.8$	$26.9 \pm 1.5$	4.6	

Table IV-2: Summary of compressive strain at room temperature tested before and after 21 days of exposure.

\* Percentage or proportion of the maximum stress achieved of porous samples concerning bulk.

### 4.3.3 Gravimetric Measurements

Figure IV-9 shows the mass variation ( $\Delta W$ ) and corrosion rate (*CR*) of NAB samples as functions of the exposure time in molten carbonate at 550 °C in aerated conditions. The B and 2G samples lose mass for a longer exposure time, and the mass quantity loss also increases, revealing a directly exponential relationship. Otherwise, the masses of the 1G, 1GHT, and 2GHT porous samples increased over time. It is important to note that 48 h could be established as a critical time, since for all samples, the corrosion rate becomes a constant value. The molten salt deposits and corrosion products formed on the surface could cause the mass gain of 1G, 1GHT, and 2GHT samples. The corrosion products can be formed by the interaction of the molten carbonate with the alloy, such as LiFeO<sub>2</sub>, or by the presence of oxygen, forming Al<sub>2</sub>O<sub>3</sub>, which has been demonstrated to be adherent to the metallic surface.



Figure IV-9: The variation of weight (a) and corrosion rate of samples (b) after 21 days (504 h) of exposure to molten salt. The samples exposed are B ( $\circ$ ), 1G ( $\Box$ ), 2G ( $\triangle$ ), 1GHT ( $\blacksquare$ ), and 2GHT ( $\blacktriangle$ ).

Audigié et al. [110] studied the corrosive behavior of aluminide and nickel-aluminide coatings in molten salts, suggesting that the aluminide coatings had a higher weight gain due to their protective effect. Therefore, the heat-treated samples (1GHT and 2GHT) had previously developed an alumina layer before exposure. Furthermore, De Miguel et al. [84] studied the corrosion behavior of the bulk alloy 51Fe-24Cr-20Ni exposed to molten carbonate at 700 °C. The authors proposed that the estimated mass loss was attributed to the lower protective properties of the oxide layer, which can also be associated with the solubility of the oxides in molten carbonates, as observed in the B and 1GHT samples, which lose mass through the exposure. Gomez-Vidal et al. [123] estimated the corrosion/protection rate according to the weight variation in alloys exposed to Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> at 750 °C, determining that it was  $1080 \pm 40 \ \mu \text{m} \cdot \text{y}^{-1}$  for In800H (30 wt.% of Ni) and  $4640 \pm 40 \text{ }\mu\text{m}\cdot\text{v}^{-1}$  for SS321 (9 wt.% of Ni). The authors [123,124] indicated that the corrosion rate was reduced, while the amount of Ni increased in the alloy. In this work, the corrosion rates were 0.1973 mm  $y^{-1}$  or 197.3  $\mu$ m  $y^{-1}$  for the B sample and 0.3742  $mm \cdot y^{-1}$  or 374.2  $\mu m \cdot y^{-1}$  for the 2G sample, which are lower than those obtained in In800H and SS321.

On the other hand, the mass gain or the positive weight is attributed to the corrosion products attached to the surface as CuO,  $Al_2O_3$ , and  $Fe_2O_3$ . According to Audigié et al. [110],  $Al_2O_3$  has better adhesion to the surface. In addition, the pore geometry of the 1G samples could have made it more difficult for corrosion products to detach from the sample.

Figure IV-10 shows a physical model of the effect of the heat treatment on the corrosion product's evolution over the surface. Before exposure, copper oxide formed clusters on all sample surfaces. In addition, the alumina oxide was generated as a cluster on the sample surface without heat treatment but as an outer layer on the sample surface with heat treatment. After exposure, the heat treatment also determined the corrosion products, forming an iron oxide caused possibly by the molten salt and metal reaction, under copper oxide, competing with aluminum oxide. The EDS analysis suggests the diffusion of iron to the surface after 21 days of exposure at high temperatures and aerated conditions, as seen in Figures IV-3 and IV-4, which simulates a real medium for an anode of exposure to this kind of anode. In addition, a greater amount of copper oxide was formed in heat-treated samples.



Figure IV-10: Physical model of the corrosion product evolution as a function of exposure time in molten salt at 550 °C in aerated conditions.

Figure IV-11 shows the XPS spectrum surveys of Al, Fe, and Cu, analyzed on surface samples before and after exposure to molten salt, with and without heat treatment. As mentioned above, the heat-treated samples formed an oxide composed of Al and Fe over the surface, which was attributed to the high reactivity of Al and Fe with the O produced in the open-to-atmosphere furnace during the heat treatment. Additionally, the heat-treated samples showed a peak of around 74 eV, which could be related to the intermetallic compounds of AlNi, which is a  $\kappa_{III}$  stable phase [124]. It is explained that the annealing provokes the martensite decomposition into the equilibrium phases. The Cu XPS survey is consistent with and without heat treatment before and after exposure because Cu is

naturally formed on the surface in the most significant proportion. It should be noted that lithium compounds were searched for in the XPS spectrum but were not found. Karfidov et al. [125] found similar results for the corrosion resistance of Monel 404 alloys (Cu-50Ni) and Hastelloy exposed to LiF–NaF–KF at 550 °C after 100 h and determined an outstanding corrosion resistance of Cu-Ni alloy under the studied conditions. Table IV-3 summarizes the changes in quantity by element produced before and after exposure. As shown, all elements decreased in the count after exposure due to the increase in O content, which was related to the oxide formed on the metal surface. The more considerable differences are in the aluminum survey, which was possibly present in the inner oxide layer, but after exposure, it is covered by iron oxide, as observed using EDS analysis. The XPS confirms an increase in the oxide amount after exposure, mainly composed of Cu, with a low amount of the other alloying elements. It has been proposed that Cu<sub>2</sub>O is a kind of copper oxide that protects against corrosion in aqueous media [126], which is present in the alloy before and after exposure but in a lower amount after exposure.



Figure IV-11: XPS survey of sample in as-built condition and heat treated before and after exposure. (a) Al, (b) Fe, and (c) Cu.

Elem.	Al				Fe				Cu			
Peak	74	l eV	76	eV	712	2 eV	724	• eV	933	eV	954	eV
Exp.	AB	HT	AB	HT	AB	HT	AB	HT	AB	HT	AB	HT
Before	0	48.9	684.1	789.5	232.8	339.7	213.6	85.6	1145.3	1291.6	680.2	734.4
After	0	142.6	279.6	393.3	131.1	335.0	27.0	116.8	954.3	1067.6	409.5	430.0

Table IV-3: Summary of chemical quantity of surface alloy elements obtained using XPS.

### 4.4 Conclusions

Bulk and porous samples were manufactured using LPBF as an anode for molten carbonate fuel cell application. The effect of annealing heat treatment and porosity on mechanical and corrosion performances was investigated. The following conclusions can be drawn from the research.

• The porosity significantly influenced the mechanical response, decreasing the maximum strength by 27% when the porosity was more than 80%. The differences fall if the porous samples present an external wall, which contributes to the strengthening of the

material. Therefore, a control in density gradient could increase the maximum strength of porous samples.

• Microstructurally, the bulk sample in its AB condition shows a great amount of martensite phase due to the quick solidification, which decreases in quantity after annealing, demonstrating a more significant amount of  $\alpha$ -phase. During exposure, the phase composition had no effect on mechanical properties since the immersion temperatures contribute to phase homogenization, and these exhibited similar mechanical properties after exposure. From a corrosion point of view, was no evidence of preferential phase corrosion.

• The heat treatment (annealing) performed before exposure produced a thin oxide layer composed principally of Al, which protected the alloy from further corrosion in contact with molten salt. However, it is unknown if the layer can influence its anode functions negatively due to the isolation that it can produce, for which a catalytic study is recommended.

• The molten salt exposure influenced the formation of the corrosion products, composed principally of Cu, Al, and Fe, whose thickness, determined using GD-OES analysis, was approximately 1.5  $\mu$ m. The 2G sample had the worst performance since it lost mass and had a corrosion rate of 0.37 mm·y<sup>-1</sup>, followed by the bulk sample that had a corrosion rate of 0.19 mm·y<sup>-1</sup>. Therefore, it is possible to conclude that the pores and their geometry affected the corrosion, since the oxides formed on the surface of these samples were not sufficiently protective or adherent.

• Regarding the suitability of Ni-Al bronze alloy fabricated through additive manufacturing as an anode for molten salt carbonate, it could be a great candidate due to its low corrosion rate compared to its counterpart and its high strength under compressive loads.

# V. CHAPTER II: THE EFFECT OF ADDING CeO<sub>2</sub> NANOPARTICLES TO Cu-Ni-Al ALLOY FOR HIGH TEMPERATURES APPLICATIONS

### 5.1 Introduction

Fuel cells (FC) are considered a promising technology for being an alternative source of electric power [127]. These devices convert chemical energy into electricity [128,129] and can be classified according to the work temperature [130]. For example, a molten carbonate fuel cell (MCFC), the operational temperature of which is 650 °C, is one of the most efficient FCs, and is contemplated as a carbon capture and storage (CSS) technology because it can capture and convert CO<sub>2</sub> [31]. The high-temperature fuel cell (600–1000 °C) uses nickel or other non-precious catalytic materials to decrease the electrode cost [131]. The electrode used as the cathode is a porous nickel oxide, where  $O_2$  and  $CO_2$  are injected, and on the anode side, nickel aluminum alloy is employed, generally Ni5Al, and supplies H<sub>2</sub>. According to the report by Lee et al. [45], a charge transfer process controls the electrochemical reactions in a slow reaction system and a mass transfer process in a rapid reaction system. Even though the MCFC has been working for decades, there are still problems to resolve due to the high operational temperature. It is essential to consider that the corrosion of the electrodes and equipment that operate at high temperatures can decrease the lifetime of FC, as Hacker and Mitsushima proposed [23]. More specifically, few works have focused on the corrosion phenomenon on the anode of MCFC. In this context, Accardo et al. [58] studied the addition of copper [68,76] and cerium oxide nanoparticles (CeO<sub>2</sub>-NPs) to improve the mechanical and electrochemical behavior of the Ni5-Al commercial anode. In this sense, as copper has good electrical and thermal conductivity and mechanical resistance [68,77], the Cu-Ni-Al alloy can be an option for the MCFC anode. On the other hand, some authors reported that incorporating CeO<sub>2</sub>–NPs in the Cu-Ni alloy increased the catalyst performance on the anode for the H<sub>2</sub> oxidation reaction [85], and incorporating it in the Ni-5Al alloy reduced the creep strain because it can keep the pore structure stable [58]. However, no available data evaluates the micro-macrostructural and corrosion behavior of a Cu-Ni-Al alloy reinforced with CeO2 nanoparticles used for the anodes in MCFC.

Therefore, the effect of nanoparticle addition on the degradation of Cu–50Ni-5Al in the electrolyte Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> (62–38 mol.%) is analyzed in this paper. The microstructural and morphological changes during this process provide valuable insights into the potential use of nanoparticles in the anode.

## 5.2 Materials and Methods

### **5.2.1 Sample Obtention**

Mechanical alloying was performed using pure powders: Nickel (<10  $\mu$ m, 99+, Merck, Darmstadt, Germany), Copper (<63  $\mu$ m, >99%, Sigma-Aldrich, Darmstadt, Germany), and Aluminum (<60  $\mu$ m, 99.9%, Good Fellow, Hamburg, Germany), which were

mechanically alloyed (MA) in a Planetary mill PQ4 Across International, obtaining powder compositions of Cu–50Ni–5A1 (wt.%). The milling conditions included a ball–a–powder ratio (BPR) of 10:1 and 2 wt.% stearic acid as a control agent under an inert Ar atmosphere. The milling time used was 100 h effective and there was an on/off cycle of 30/15 min at a speed of 350 r.p.m. Subsequently, 1, 3, and 5 wt.% of the nanoparticles CeO<sub>2</sub> (CeO<sub>2</sub>–NPs) (<25 nm, >99.9%, Sigma-Aldrich, Hamburg, Germany) were added to the alloy using Mixer Y–type Astecma for 1 h. Table V-1 shows the chemical composition of Cu–50Ni–5Al + xCeO<sub>2</sub> (wt.%) alloys.

Sample	Cu	Ni	Al	CeO <sub>2</sub>
0 wt.% CeO <sub>2</sub> -NPs	Bal.	50	5	0
1 wt.% CeO <sub>2</sub> –NPs	Bal.	50	5	1
3 wt.% CeO <sub>2</sub> –NPs	Bal.	50	5	3
5 wt.% CeO <sub>2</sub> -NPs	Bal.	50	5	5

Table V-1: Chemical composition of the Cu-50Ni-5Al + xCeO<sub>2</sub> (wt.%) alloys.

Cu-50Ni-5Al without and with the CeO<sub>2</sub>-NPs samples were consolidated by Spark Plasma Sintering (SPS) using a Fuji Electronic Industrial Co model DR. SINTER<sup>®</sup> SPS1050. The disks were 10 mm in diameter and 7 mm in thickness and were produced using a high-density graphite die. The samples were heated from room temperature to 800 °C at a heating rate of 100 °C min<sup>-1</sup>, applying a pressure of 50 MPa simultaneously during the heating and holding time of 5 min at the sintering temperature. The entire SPS process was kept under a vacuum of approximately 20 Pa. Finally, the samples were free-cooled to room temperature at a cooling rate of roughly 10 °C s<sup>-1</sup> in the SPS chamber. Figure V-1 shows the sample preparation (powders) diagram by mechanical alloying and mechanical mixing and a schematic representation of the consolidation process by the SPS system.

The metal samples were polished using sandpaper from #800 to #4000 and then with colloidal silica suspension to reveal their microstructure. The polished samples were rinsed with ethanol for 10 min in a bath cleaning sonicator. Afterward, the samples were cleaned with distilled water and dried at room temperature.



Figure V-1: Sample preparation (powder mixture) and schematic representation of the SPS system (consolidation).

### 5.2.2 Gravimetric Measurements

The Cu–50Ni–5Al samples were immersed in molten eutectic Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> (62–38 mol.%) [55,57] for 504 h (21 days) in an aerated atmosphere or not–controlled medium at 550  $\pm$  5 °C. The gravimetric measurements of samples were carried out as described previously by Arcos et al. [132]. The samples were removed and cleaned to eliminate the deposits and corrosion products on the surface. The bulk samples were submerged in hot distilled water (~100 °C) in a sonicator bath (Elma D–78224 Singen/Htw) for 30 min. Subsequently, the samples were dried with hot air and weighed until they reached a constant value, as reported by the ASTM G1–03 [92]. The average mass (%) was calculated using Equation (V.1).

$$\frac{m_i - m_f}{m_i} \times 100 \tag{V.1}$$

where m<sub>i</sub> and m<sub>f</sub> are the initial and final sample masses at different exposure times.

### 5.2.3 Morphological and Chemical Characterization

The porosity was determined through Archimedes' method, according to the Standard Test ASTM C373–88 [99]. To reveal the microstructure, an etching was employed: 5 g of Fe<sub>3</sub>Cl, 10 mL of HCl, and 100 mL of distilled water for 8 s. A field–emission scanning electron microscope (FE-SEM), QUANTA FEG 250, was used to obtain the samples' images.

X-ray diffraction (XRD) was implemented using Bruker D2 PHASER with Cu– $K\alpha$  radiation to characterize the material's structure. The diffraction patterns were recorded from 20 between 40° and 100° with a 0.02° step and counting time of 1 s/step.

## 5.2.4 Mechanical Characterization

The microhardness of the samples was calculated by a micro–Vickers durometer, Wilson<sup>®</sup> VH1150 Macro Vickers Hardness Tester, under 0.3 kgf of force before the gravimetric measurements.

## **5.2.5 Electrochemical Measurements**

The electrochemical behavior of the Cu–50Ni–5Al samples was studied using open circuit potential and electrochemical impedance spectroscopy (EIS) measurements in the molten Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> (62:38 mol.%) as an electrolyte at 550 ± 5 °C under an aerated atmosphere. The electric contact for the working electrode, the Cu–50Ni–5Al samples, was performed using conductive silver printing ink (resistivity 5–6  $\mu\Omega$  cm) around the sample and copper wire of 25 cm in length. In addition, a Pt wire that was 25 cm in length was used as a counter electrode, and an Ag wire that was 25 cm in length and placed inside a quartz glass tube with a porous plug in the tip was used as the reference electrode. The electrochemical measurements were carried out with a Potentiostat Solartron Analytical.

## 5.3 Results and Discussion

## **5.3.1 Gravimetric Measurements**

Figure V-2 shows the effect of CeO<sub>2</sub>–NPs on the weight gain of the Cu–50Ni–5Al samples after exposure to molten carbonates, revealing a reduction in the weight by adding CeO<sub>2</sub>–NPs. In addition, Figure V-2 shows that during the initial stage, the weight increased rapidly for all the Cu–50Ni–5Al samples, which was lower for Cu–50Ni–5Al + 1 wt.% CeO<sub>2</sub>–NPs, reaching a maximum weight gain of only 1.2% at 504 h of exposure. For a longer exposure time, the weight gain reaches a stationary state associated with a passive oxide layer [132] formed after 80 h for Cu–50Ni–5Al + 3 wt.% CeO<sub>2</sub>–NPs, and after 160 h for Cu–50Ni–5Al + 0 wt.% CeO<sub>2</sub>–NPs. It should be noted that with 5 wt.% CeO<sub>2</sub>–NPs, the weight gain did not reach a plateau of up to 504 h of exposure, like the sample with 3 wt.% CeO<sub>2</sub>–NPs. Therefore, the sample that suffered the least degradation at high temperatures was 1 wt.% CeO<sub>2</sub>–NPs.



Figure V-2: The variation of weight of Cu−50Ni−5Al samples after 504 h of exposure to molten carbonates. (●) 0 wt.% CeO<sub>2</sub>−NPs, (■) 1 wt.% CeO<sub>2</sub>−NPs, (▲) 3 wt.% CeO<sub>2</sub>−NPs, (▲) 5 wt.% CeO<sub>2</sub>−NPs.

### 5.3.2 Microstructural and Chemical Characterization

Figure V-3 shows the morphology of the samples before and after 504 h of exposure to molten carbonate ( $Li_2CO_3-K_2CO_3$  62–38 mol.%) in the aerated atmosphere. Before exposure, porosity can be observed for all the samples, agreeing with the analysis performed. For example, Cu-50Ni-5Al had  $16 \pm 0.8\%$  porosity, which reduced the addition of CeO<sub>2</sub>–NPs. The Cu–50Ni–5Al + 1 wt.% CeO<sub>2</sub>–NPs samples had  $1.0 \pm 0.3\%$ porosity, Cu-50Ni-5Al + 3 wt.% CeO<sub>2</sub>-NPs had  $2.0 \pm 0.2\%$  porosity, presenting some spots more lightly over the surface, and Cu-50Ni-5Al + 5 wt.% CeO<sub>2</sub>-NPs had  $1.0 \pm$ 0.1% porosity. One reason for this phenomenon is that nanoparticles can easily remain in the pores and voids of the nanocomposite matrix due to their small size [133]. After exposure, a strong surface modification was observed for all the samples, possibly due to the corrosion product formation, which could be a passive film, as suggested by the gravimetric measurements. Ren et al. [82] studied a Cu-35Ni-10Al alloy in molten carbonate (Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> 62–38 mol.%) for 48 h in an aerated atmosphere, reporting the formation of porous corrosion products composed mainly of Al<sub>2</sub>O<sub>3</sub> and Ni–Al oxides, which is in agreement with the SEM images of Cu-50Ni-5Al (see Figure V-3a), which present a porous surface after exposure.



Figure V-3: FE–SEM images before Cu–50Ni–5Al: (a) 0 wt.% CeO<sub>2</sub>–NPs, (b) 1 wt.% CeO<sub>2</sub>–NPs, (c) 3 wt.% CeO<sub>2</sub>–NPs, (d) 5 wt.% CeO<sub>2</sub>–NPs, and after gravimetric measurements Cu–50Ni–5Al, (e) 0 wt.% CeO<sub>2</sub>–NPs, (f) 1 wt.% CeO<sub>2</sub>–NPs, (g) 3 wt.% CeO<sub>2</sub>–NPs, and (h) 5 wt.% CeO<sub>2</sub>–NPs.

Figure V-4 presents the EDS results before and after exposure to analyze the chemical composition of the sample's surface. Before exposure, the alloy's surface is very similar for all the samples, revealing a homogeneous distribution of all the elements (Cu, Ni, Al, and O). However, Cu-50Ni-5Al has some Al spots, and Cu-50Ni-5Al + 3 wt.%  $CeO_2$ -NPs have some zones not identified by the mapping, which could be Li because it has deficient energy and is difficult to detect. Cu-50Ni-5Al+ 5 wt.% CeO<sub>2</sub>-NPs present some nanoparticles agglomeration (CeO<sub>2</sub>) corresponding to the element Ce. Frattini et al. [134] observed the same effect when adding small amounts of ZrO<sub>2</sub>-NPs in the Ni-Al alloy, although, with the increase in the amount to 10% ZrO<sub>2</sub>–NPs, the distribution of the NPs becomes homogeneous. After exposure, the quantity of oxygen (O) increased significantly for all the samples, which can be attributed to the oxide formation on the surface, as proposed above. Nevertheless, potassium (K) was also found on the surface, a component of the molten carbonates (Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>), revealing the possible formation of a deposit. According to Gonzalez-Rodriguez et al. [135], the Ni-50Al alloy was immersed in Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> (62:38 mol%) for 100 h in static air at 650 °C. They reported that the main corrosion products were Ni, Al, and K, such as NiO, Al<sub>2</sub>O<sub>3</sub>, LiAlO<sub>2</sub>, and LiKCO<sub>2</sub>. Also, Ren et al. [82] described mainly Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O as the corrosion products of Cu-35Ni-10Al exposure to  $Li_2CO_3$ -K<sub>2</sub>CO<sub>3</sub> (62:38 mol%) during 1 h in air at 650 °C. Accardo et al. [58] also proposed that CeO<sub>2</sub>-NPs could migrate from the alloy to the electrolyte. EDS analysis revealed a slight decrease in the Ce content for the Cu-50Ni-5Al + 5 wt.% CeO<sub>2</sub>-NPs sample. For the other samples, the Ce content increases, which can be associated with diffusion from the bulk to the surface of the molten carbonates.



Figure V-4: EDS surface mapping before Cu-50Ni-5Al: (a) 0 wt.% CeO<sub>2</sub>-NPs, (b) 1 wt.% CeO<sub>2</sub>-NPs, (c) 3 wt.% CeO<sub>2</sub>-NPs, (d) 5 wt.% CeO<sub>2</sub>-NPs and after gravimetric measurements Cu-50Ni-5Al; (e) 0 wt.% CeO<sub>2</sub>-NPs, (f) 1 wt.% CeO<sub>2</sub>-NPs, (g) 3 wt.% CeO<sub>2</sub>-NPs, and (h) 5 wt.% CeO<sub>2</sub>-NPs.

Figure V-5 compares the XRD patterns recorded before and after exposure to  $Li_2CO_3-K_2CO_3$  (62:38 mol%). Before exposure, the reflections were identified as corresponding to typical fcc structures (Fm-3m). No peaks were associated with Ni or Al, indicating that the solid solution Cu-Ni-Al obtained by mechanical alloving is maintained post-sintering by SPS. The samples reinforced with CeO<sub>2</sub>-NPs show lowintensity reflections associated with CeO<sub>2</sub> (Fm-3m; JCPDS 010750076). The lattice parameter of the Cu-Ni-Al alloys without CeO<sub>2</sub>-NPs is 0.358 nm, which remains constant when incorporating the different CeO<sub>2</sub>–NPs. This indicates that the CeO<sub>2</sub>–NPs do not react with the Cu-Ni-Al matrix in the consolidation process because the SPS technique is a fast method for sintering [136]. After 21 days of exposure to the Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>, peaks associated with NiO (Fm-3m; JCPDS 010731519), Cu<sub>2</sub>O (Pn-3m; JCPDS 010751531), and Al<sub>2</sub>O<sub>3</sub> (R-3c; JCPDS 010772135) can be seen in all the samples. In addition, the intensities of the reflections associated with CeO<sub>2</sub>–NPs can be seen, which can be attributed to the fact that the CeO<sub>2</sub>-NPs migrate to the surface, as reported by Accardo et al. [58]. Note that the increase in the intensity of the reflections associated with CeO<sub>2</sub> is much lower for the sample with 5 wt.% of CeO<sub>2</sub>–NPs than in the samples with 1 wt.% and 3 wt.% of CeO<sub>2</sub>–NPs, possibly because the Ce content decreased on the sample surface, confirming what was previously mentioned in Figure V-4.



Figure V-5: XRD patterns of Cu-50Ni-5Al samples: (a) 0 wt.% CeO<sub>2</sub>-NPs, (b) 1 wt.% CeO<sub>2</sub>-NPs, (c) 3 wt.% CeO<sub>2</sub>-NPs, (d) 5 wt.% CeO<sub>2</sub>-NPs before and after gravimetric measurements.

### **5.3.3 Mechanical properties**

Figure V-6 shows the hardness of the Cu–50Ni–5Al + x wt.% CeO<sub>2</sub>–NPs samples before exposure. The results indicate that the sample with 0% CeO<sub>2</sub>–NPs presents the lowest hardness value, corresponding to  $205 \pm 21$  HV<sub>0.3</sub>. This can be attributed to the higher porosity of the sample, which reaches 16%, by incorporating different amounts of CeO<sub>2</sub>–NPs in the sample. Cu–50Ni–5Al +1 wt.% CeO<sub>2</sub>–NPs perform better due to the CeO<sub>2</sub>–NPs allowing a decrease in the porosity and a homogenous distribution of CeO<sub>2</sub>–NPs in the matrix, as mentioned above. However, if the concentration of CeO<sub>2</sub>–NPs exceeds 1 wt.%, they agglomerate at grain boundaries, reducing the hardness value, as seen in Figure V-6. Zawrah et al. [137] concluded that adding Al<sub>2</sub>O<sub>3</sub>–NPs to pure Cu improves hardness due to their uniform distribution. The improved hardness can be attributed to the relative contribution of the Orowan strengthening effect, mainly when the reinforcement size is less than 100 nm [138]. The CeO<sub>2</sub>–NPs are very small and hard, impeding the movement of dislocations in the Cu–50Ni–5Al matrix, leading to an improvement in the hardness of the microstructure.



Figure V-6: Microhardness of the samples Cu−50Ni−5Al: (●) 0 wt.% CeO<sub>2</sub>−NPs, (■) 1 wt.% CeO<sub>2</sub>−NPs, (♦) 3 wt.% CeO<sub>2</sub>−NPs, (▲) 5% wt.% CeO<sub>2</sub>−NPs before exposure.

### 5.3.4 Electrochemical measurements

Figure V-7 shows the effect of the addition of 1 wt.% CeO<sub>2</sub>–NPs to the open circuit potential (E<sub>OC</sub>) of Cu–50Ni–5Al after exposure to  $Li_2CO_3-K_2CO_3$  at 550 °C and an aerated atmosphere. After a shorter exposure time, the E<sub>OC</sub> was shifted to more negative values by incorporating CeO<sub>2</sub>–NPs, suggesting an activation of the corrosion phenomena. However, for a longer exposure time, the E<sub>OC</sub> reached similar values to the sample without CeO<sub>2</sub>–NPs, which can be associated with a stable oxide layer formed on the metal surface. Meléndez-Ceballos et al. [139] studied a Ni porous sample coated by CeO<sub>2</sub>–NPs using the atomic layer deposition in Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> at 650 °C in a CO<sub>2</sub>/air 30/70 vol.% atmosphere. The authors determined an initial potential close to -0.76 V vs. Ag/Ag<sup>+</sup>; the reference electrode is a silver wire submerged in Ag<sub>2</sub>SO<sub>4</sub> (10<sup>-1</sup> mol kg<sup>-1</sup>) saturated in Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>, which was shifted to more positive values as a function of exposure time, attributed to a delay in the Ni oxidation process due to the presence of CeO<sub>2</sub>–NPs film.



Figure V-7: Open circuit potential variation of (●) Cu-50Ni-5Al and (■) Cu-50Ni-5Al + 1 wt.% CeO<sub>2</sub>-NPs exposure to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> at 550 °C and aerated atmosphere over time.

Figure V-8 shows the Nyquist diagrams of Cu–50Ni–5Al after 1 h of exposure to  $Li_2CO_3-K_2CO_3$  in an aerated atmosphere at  $E = E_{OC}$  and 550 °C, revealing a significant increase in the impedance modulus due to the incorporation of 1 wt.% CeO<sub>2</sub>–NPs, which could be related to the formation of a passive oxide layer on the alloy, as previously mentioned. As can be seen at  $E = E_{OC}$ , the impedance responses reveal two time constants at high and low frequency ranges (HF and LF), which can be associated with the cathodic current, not only involving the capacitance of the electric double layer (Cdl) and the oxygen reduction reaction, but also the formation of an oxide layer due to the alloy dissolution. Different equivalent circuits have been proposed to represent the physical model, which can be composed of capacitors, resistances, and constant phase elements (CPE) related to the heterogeneity of the surface [140].



Figure V-8: Nyquist diagrams of (a) Cu–50Ni–5Al and (b) Cu–50Ni–5Al + 1 wt.% CeO<sub>2</sub>–NPs exposure 1 h to  $Li_2CO_3$ –K<sub>2</sub>CO<sub>3</sub> at 550 °C, aerated atmosphere, and E = E<sub>OC</sub>.

Figure V-9 shows the Bode plots of Cu–50Ni–5Al + 1 wt.% CeO<sub>2</sub>–NPs after 1 h of exposure to  $Li_2CO_3$ –K<sub>2</sub>CO<sub>3</sub> in an aerated atmosphere at E = E<sub>OC</sub> and 550 °C, as a representative example of the study system. Figure V-9 reveals a capacitive response with

two or three time constants at all frequency ranges, possibly associated with the formation of an oxide film and oxygen reduction reaction. Additionally, the Bode plots revealed a higher impedance modulus at the LF range when  $CeO_2$ -NPs were added, which can be related to the polarization resistance of the system, suggesting an enhancement of the corrosion resistance due to the incorporation of the  $CeO_2$ -NPs to the Cu-50Ni-5Al matrix [140–142]. Moreover, Figure V-9 shows the non-corrected (**■**) and corrected Bode plots by electrolyte resistance ( $\Box$ ), revealing that this effect is mainly in the high frequency range.



Figure V-9: (a,b) Effect of correction of electrolyte resistance on Bode plots and (c) variation of the imaginary part of the impedance of Cu-50Ni-5Al + 1% wt.% CeO<sub>2</sub>-NPs exposure 1 h to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> in aerated atmosphere at 550 °C and  $E = E_{OC}$ .

Figure V-c shows the variation of the imaginary part of the impedance of Cu–50Ni–5Al + 1 wt.% CeO<sub>2</sub>–NPs as a function of frequency after 1 h of exposure to Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> in an aerated atmosphere at  $E = E_{OC}$  and 550 °C, revealing a constant phase element (CPE) behavior in the MF range, with a negative slope ( $\alpha$ ) that varied between -0.33 ± 0.01 for Cu–50Ni–5Al and -0.65 ± 0.004 for Cu–50Ni–5Al + 1% wt.% CeO<sub>2</sub>–NPs, which can be related to the oxide film formed on the metal surface and described by the following relation, as reported by Orazem and Tribollet [143], Tribollet et al. [144], and Hirschorm et al. [145].

$$Z_{oxide} = \int_0^\delta \frac{\rho(\gamma)}{1 + j\omega\rho(\gamma)\varepsilon(\gamma)\varepsilon_0} d\gamma$$
(V.2)

The authors proposed the power-law model (PLM) to analyze the film properties using Equation (4.3):

$$Z(\omega) = g \frac{\delta \rho_{\delta}^{1-\alpha}}{(\rho_0^{-1} + j\omega\varepsilon\varepsilon_0)^{\alpha}}$$
(V.3)

In this case,  $\alpha$  is the slope in the Log  $Z_{Imag}$  vs. Log f plots,  $\varepsilon$  represents the dielectric constant of the oxide layer formed on the metal alloy,  $\varepsilon_0$  is the vacuum permittivity that

is equal to  $8.85 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$ , and g is a numerical coefficient close to 1 when  $\alpha$  is 1, which can be estimated using the following equation:

$$g = 1 + 2.88 (1 - a)^{2.375}$$
(V.4)

In addition,  $\rho_0$  and  $\rho_\delta$  represent the lower and upper limits in the frequency range where CPE behavior is observed. The Q value corresponds to a CPE parameter that can be determined using the following equation:

$$Q = \frac{(\varepsilon \varepsilon_0)^{\alpha}}{g \delta \rho_{\delta}^{1-\alpha}} \tag{V.5}$$

The graphical method of the impedance data allowed us to estimate the CPE parameters for the Cu–50Ni–5Al Q coefficient of  $1.62 \times 10^{-3}$  F·cm<sup>-2</sup>·s<sup>-(1- $\alpha$ )</sup> and  $|\alpha|$  value of 0.60, and for the Cu–50Ni–5Al + 1% wt.% CeO<sub>2</sub>–NPs, the Q coefficient of  $6.95 \times 10^{-3}$  F·cm<sup>-2</sup>·s<sup>-(1- $\alpha$ )</sup> and  $|\alpha|$  value of 0.67. Furthermore, electrolyte resistance (*Re*) was determined by the graphical method, finding values close to 2.7  $\Omega$  cm<sup>2</sup> for Cu–50Ni–5Al and 0.84  $\Omega$  cm<sup>2</sup> for the Cu–50Ni–5Al + 1% wt.% CeO<sub>2</sub>–NPs samples. Those parameters reveal that the addition of CeO<sub>2</sub>–NPs to Cu–50Ni–5Al improves the corrosion resistance, possibly due to a lower porosity of the oxide film or a thicker oxide layer.

### 5.4 Conclusions

The Cu–50Ni–5Al alloys were obtained by mechanical alloying and the SPS process, which allowed the addition of CeO<sub>2</sub>–NPs into the metal matrix. The samples were exposed to molten carbonate (Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>), consequently forming corrosion products over the surface, which were analyzed by SEM-EDS and corroborated by X–ray diffraction. The addition of CeO<sub>2</sub>–NPs in the Cu–50Ni–5Al matrix reduced the mass variation over time, mainly using 1% wt. CeO<sub>2</sub>, reaching a maximum weight gain of only 1.2% at 504 h of exposure. The corrosion products were composed of nickel oxide, aluminum oxide, and copper oxide in all the alloys, regardless of the amount of NPs incorporated.

Moreover, the microhardness significantly increased for the alloy containing 1 wt.% of  $CeO_2$ -NPs, reaching a hardness value of 340 HV0.3. Furthermore, the impedance analysis revealed that the samples with 1 wt.% of  $CeO_2$ -NPs in the molten carbonates in an aerated atmosphere had a higher impedance modulus, possibly due to the lower porosity of the oxide film or a thicker oxide layer.

Therefore, the alloys that showed better mechanical behavior and higher corrosion resistance were Cu-50Ni-5Al + 1 wt.%  $CeO_2-NPs$ , which have a promissory use at high temperatures.

## VI. CHAPTER III: CORROSION BEHAVIOR OF Ni-AI BRONZE BY LPBF IN MOLTEN CARBONATES

### 6.1 Introduction

The molten salts can transfer heat energy during the phase change from solid at room temperature into a liquid state at high temperature, making them suitable for thermal energy storage. In energy transmission, concentrated solar power plants (CSP) and fuel cells frequently use molten salts [146]. Different types of these salts, such as binary, ternary, and quaternary, a combination of sodium, potassium nitrate, and lithium, are tailored to meet different requirements, such as achieving a desired melting point [147–151]. Despite their advantages, molten salts are stored in tanks and moved in their liquid state through metallic components, including pumps, pipelines, and cells, which can rapidly deteriorate these components due to their corrosive nature and operating temperature.

Several alloys exposed to molten salt have been studied to improve the corrosion of alloys and to understand the corrosive mechanisms to implement effective mitigation strategies. Table VI-1 summarizes alloys-molten carbonate systems that have been previously investigated, such as F. Pineda et al. [140], who studied the corrosion process of ASTM A36 and AISI 304L exposed to NaNO3-KNO3 (60 - 40 wt.%) at 390 °C using electrochemical techniques for 21 days. The researchers analyzed the evolution of the oxide layer formed on metal surfaces. The authors determined that the oxide film was more porous on ASTM A36 and more passive and uniform on AISI 304L, reaching stability after 14 days of exposure with a thickness close to 1.5 nm. L. González-Fernández et al. [151] investigated mitigation strategies for SS310 exposed to molten ternary carbonate salt (Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>) at 600 °C for 25 days. In their approach, the sample surface was laser-treated before immersion into the molten carbonate salt. The study demonstrated that this treatment induced the adhesion of organic groups in the form of hydrocarbons, facilitating the formation of denser corrosion products and enhancing the protection of the oxide layer. A. Fernández et al. [152] compared In702 and 304L exposed to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> at 550 °C during 1,000 h, determining the best corrosion resistance of In702 due to the passive layer formed in the surface composed by Al<sub>2</sub>O<sub>3</sub> and NiCr<sub>2</sub>O<sub>4</sub>. Therefore, the alloys and their compounds determine the protective properties of the oxide layer formed on the metal surface.

Metal alloy	Molten carbonates	T (°C)	Ref
316SS	Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (33–29–38 mol%)	600	[153]
Ni-based IN702	Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (30–57–13 mol%)	550	[152]
HR224	Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (32–35–33 mol%)	650	[153]
Ni11Fe10Cu	K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (41–59 mol%)	720	[154,155]
Fe-Cr-Al	K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (48–52 wt%)	800	[156]
310SS	Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (32–35–33 wt%)	600	[150]
347SS	Li <sub>2</sub> CO <sub>3</sub> -K <sub>2</sub> CO <sub>3</sub> -Na <sub>2</sub> CO <sub>3</sub> (32–35–33 wt%)	600	[147]
304L	$NaNO_3$ - $KNO_3 (60 - 40 \text{ wt\%})$	390	[140]

Table VI-1: Metal alloys exposed to high temperatures.

Cu alloys can be an alternative material at high temperatures due to their high corrosion resistance, which is related to a protective oxide layer formed on their surface, and they have a low price. For example, Peressi et al. [157] studied the corrosion behavior of a brass exposed to an ionic liquid at 150 °C for 48 h of immersion, finding a low corrosion current close to Inconel. Feng and Melendres [158] exposed different metal oxides, such as Cu, Ni, Fe, Co, and Mo, to molten LiCl-KCl (44.2-55.8 wt.%) between 375-450 °C for cathode battery application, reporting that passivating layer formed on the surface reach in Fe, Ni. The authors determined a reduction in the reversibility for Fe, Co, and Cu oxides, quasi-reversibility for Ni oxide, and irreversibility for Mo oxide. Arcos et al. [132] studied Cu-11Al-5Ni-4Fe wt.% alloy (NAB) exposed to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> at 550 °C for 21 days, finding that a protective layer forms on the surface composed of CuO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> which a delay in the corrosion process. Additionally, NAB alloy has demonstrated advantages over other alloys regarding corrosion performance exposed to NaCl at room temperature, making it suitable for marine environments [132]. However, until now, it has been unclear if copper alloy can be a candidate for pipeline or heater in contact with molten salts.

Therefore, this work aims to compare the corrosion behavior of a nickel-aluminum (Ni-5Al) and a nickel-aluminum bronze (NAB) after exposure to molten carbonate at high temperature. The study was carried out using electrochemical impedance spectroscopy for monitoring the corrosion behavior, the scanning electron microscope and X-ray photoelectron spectroscopy for understanding the evolution of the oxide layer before and after exposure.

## 6.2 Materials and Methods

## 6.2.1 Sample fabrication

The Ni-5Al wt.% alloy powder (<45  $\mu$ m, Sichuan Porous Metal Technology CO, LTD) and NAB alloy composed of Cu-11Al-5Ni-4Fe wt.% alloyed powder (<40  $\mu$ m, CNPC powder group CO) were manufactured using LPBF technique (GE - Concept Laser <u>Mlab</u> using 200R machine), with a laser power of 180 W, a scanning speed of 600 mm·s<sup>-1</sup>, and using 30  $\mu$ m and 80  $\mu$ m for the layer thickness and hatch space. The total volumetric energy density (VED) was 125 J·mm<sup>-3</sup>. Thus, cylindrical samples were fabricated with 6 mm height and 8 mm diameter, constructed over a 100 x 100 mm stainless steel and copper platform, respectively. Then, the samples were mechanically polished using grit sandpapers (#400 to #4000) and colloidal silica suspension.

## 6.2.2 Microstructure analysis

Before exposure, Ni-5Al and NAB samples were etched using immersion for 8 s in a ferritic solution composed of 5 g Fe<sub>3</sub>Cl, 10 mL HCl, and 100 mL distilled water. Then, samples were cleaned with distilled water and alcohol and dried using compressed air. The microstructure was analyzed using optical images (Olympus SC50).

## 6.2.3 Surface analysis

Before and after exposure, the morphology surface of Ni-5Al and NAB samples was investigated using a field emission-scanning electron microscope using a QUANTA FEG 250 FE-SEM. Both alloy samples were also analyzed by X-ray photoelectron spectroscopy (XPS), and spectra were measured using a hemispherical analyzer (Physical Electronics 1257 system). A twin anode (Mg and Al) X-ray source was operated at a constant power of 200 W using Al K $\alpha$  radiation (1486.6 eV) for measurements. The alloys were placed in a sample stage where the emission angle was fixed at 15° and the pressure during the spectrum acquisition was kept in the range of 10<sup>-9</sup> mbar. Before the spectral analysis, the binding energy (BE) was calibrated with the adventitious carbon C1s signal centered at 284.6eV. Also, a Shirley background subtraction was applied to all the spectra [159].

## **6.2.4 Electrochemical measurements**

The electrochemical measurements were performed using a potentiostat/galvanostat (Solartron Analytical Xm) and a three-electrode electrochemical cell. Ni-5Al and NAB samples were used as working electrodes with a geometrical area of 1.16 cm<sup>2</sup> and 1.08 cm<sup>2</sup>. A wire Au was employed as the counter electrode. A silver wire dipped into an Ag<sub>2</sub>SO<sub>4</sub> (10<sup>-1</sup> mol·kg<sup>-1</sup>) saturated Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub> (68:32% mol) contained in an alumina tube sealed by a porous alumina membrane was used as the reference electrode [93]. The test was performed under air-free conditions, with a constant flow of H<sub>2</sub>/N<sub>2</sub> in a 40/10 ml·min<sup>-1</sup> ratio. The electrolyte was a molten carbonate (Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>,68:32% mol) kept at 550 °C. The open circuit potential and impedance data were collected during five days of exposure. The electrochemical impedance spectroscopy (EIS) was measured in duplicates between 65 kHz and 3 mHz, using eight points per decade and an amplitude of 10 mV at E = E<sub>OC</sub> and E = E<sub>OC</sub> ± 30 mV.

## 6.3 Results and discussion

## 6.3.1 Microstructure characterization

Figure VI-1 shows the optical image of Ni-5Al and NAB alloy before exposure, revealing the grain boundary for Ni-5Al alloy, which corresponds to a single phase ( $\gamma$ -FCC), as previously reported by Özel and Arisoy [160] and Ponomaryova et al. [161]. Figure VI-1(b) shows the NAB alloy with martensite microstructure and some precipitated related to the  $\kappa$ -phase, as previously reported by our research group [132], with grain sizes close to 30 µm and 25 µm, respectively. The porosity of Ni-5Al was 3 ± 0.3 %, and density of 8 ± 0.01 g·cm<sup>-3</sup>; for the NAB alloy, the porosity was 3.5 ± 1.7 % and density of 7.5 ± 0.05 g·cm<sup>-3</sup>. Previously, our group reported that the NAB sample manufactured by LPBF was mainly composed of an  $\alpha$ -cubic phase, which consists primarily of copper,  $\beta$ ' phase, representing a martensite structure, and the  $\kappa$ -phase, which comprises intermetallic combinations of various alloying elements, including Fe-rich components, such as Fe<sub>3</sub>Al/FeAl [132].



Figure VI-1: Micrograph of (a) Ni-5Al and (b) NAB alloys before exposure.

### 6.3.2 Surface analysis

Figure VI-2 shows the FE-SEM images of both alloys before and after 5 days of exposure to molten carbonates (Li<sub>2</sub>CO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>) under a controlled atmosphere H<sub>2</sub>/N<sub>2</sub> in a 40/10 mL·min<sup>-1</sup> ratio. Before exposure, both alloys revealed that the alloying elements were homogeneously distributed over the surface. For example, the EDX determined that Figure VI-2 (b) Ni (96 wt.%), Al (4 wt.%) whose values follow the alloy Ni-5Al wt.%, and Figure VI-2 (d) Cu (67 wt.%), Al (17 wt.%), Fe (9 wt.%), and Ni (7 wt.%), whose values are similar to the commercial NAB alloy Cu-11Al-5Ni-4Fe wt.%. After 5 days of exposure, Figure VI-2(e,f) shows some molten carbonate clusters formed on the Ni-5Al surface, composed mainly of potassium (K). The EDX corroborates it because, in Figure VI-2(f), appears the K (in a 5 wt.%), in purple color. On the other hand, Figure VI-2(g,h) the NAB sample shows a more roughened surface, composed of molten carbonates and iron (Fe), where the EDX indicates that in Figure VI-2(h), the amount of K (13 wt.%) appear on the surface and the amount of Fe (42 wt.%) increase compared to the beginning. This increase of Fe over the surface could be due to the formation of LiFeO<sub>2</sub> as a corrosion product described by De Miguel et al.[84] and Wang et al. [146].



Figure VI-2: FE-SEM and EDS analysis of (a,b,e,f) Ni-5Al and (c,d,g,h) NAB (e-h) samples. (a-d) Before and (e-h) after exposure to molten carbonate at 550 °C. (a,c,e,g) Backscattering and (b,d,f,h) mapping.

Figure VI-3(a) shows the XPS completed spectrum of Ni-5Al and NAB alloys after exposure to molten carbonates. The deconvolution of the peaks related to Li 1s, K 1s, Ni 2p, Al 2p, and Cu 2p revealed the deposits of Li<sub>2</sub>CO<sub>3</sub> (55.58 eV [162,163]) and K<sub>2</sub>CO<sub>3</sub> (292.57 and 293.65 eV [164,165]) over the surface on both samples, as shown in Figure VI-3(b,c). This could occur because the samples were not cleaned after being removed from the molten carbonates mixture. This was to avoid interfering with the surface analysis, then were stored in a desiccator. Figure VI-3(d) shows the Al 2p signal in both samples. For the Ni-5Al sample, the Al 2p signal appears as metal Al (74.05 eV [166]) and Al<sub>2</sub>O<sub>3</sub> (75.89 eV [166,167]), as can be seen in Figure VI-3(e). The low intensity of the alumina oxide signal in this alloy can be related to the small amount within the alloy.

For NAB alloy, the predominant signal is associated with Al<sub>2</sub>O<sub>3</sub> (74.11 eV [166–168]), which also appears in the deconvolution of [29] Al(OH)<sub>3</sub> (532 eV [168]), as also seen in Figure VI-3(f). Therefore, it is expected that a passive layer was formed on the NAB surface. Ni 2p signal was identified in the Ni-5Al sample, which was in the form of nickel oxide hydroxide NiO(OH) (856.01 eV and 857.43 eV [169–171]), as shown in Figure VI-3 (e). These results are in concordance with several authors, who proposed that NiO, NiO(OH), and Ni(OH)<sub>2</sub> are suitable materials to be used as electrodes in fuel cells and batteries due to their catalytic properties [172–174]. For NAB alloy, the Ni 2p signal was not detected by XPS analysis, suggesting that this element was not incorporated into the corrosion products formed during exposure. For NAB alloy, a Cu 2p signal appears as copper (I) oxide (932.22 eV [175,176]) with greater intensity than copper (II) oxide (933.99 eV [175,176]). Therefore, the corrosion product formed on NAB alloy mainly comprises copper oxide (I) and aluminum oxide.



Figure VI-3: XPS spectra of Ni-5Al (b-e) and NAB (b-c,f-g) alloys after exposure to molten carbonate. A complete spectrum (a), (b-c) Li 1s and K 2p, (d-e) Al 2p and Ni 2p, (f-h) O 1s, Cu 2p, and Al 2p.

It is worth mentioning that Grosu et al. [147] and González-Fernández et al. [150] found that Li(Fe, Ni)<sub>5</sub>O<sub>8</sub> and Li(Fe, Ni)O<sub>2</sub> over the surface in SS310 alloy exposed to Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> as corrosion products. Also, Pineda et al. [140] described that the corrosion product Fe<sub>3</sub>O<sub>4</sub> was generated on the surface of 304L alloy exposed to NaNO<sub>3</sub>-KNO<sub>3</sub>. On the other hand, Férnandez and Cabeza [152] and Fernández et al. [155] reported the formation of Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-Li<sub>2</sub>CO<sub>3</sub> on In 702 and HR22 alloys after exposure to molten carbonate. The authors also described the formation of corrosion products on the metal surfaces, such as Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, and NiO. Additionally, Yang et al. [155] described that a passive film of NiO and NiFe<sub>2</sub>O<sub>4</sub> was formed on Ni11Fe10Cu after exposure to Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>.

### 6.3.3 Electrochemical behavior

Figure VI-4 shows the evolution of the open circuit potential ( $E_{oc}$ ) of Ni-5Al and NAB after exposure to molten carbonates at 550 °C. Ni-5Al shows an increment of the  $E_{oc}$  during earlier stages of exposure, then decreases slightly to increases again, from -0.68 to -0.4 V vs. Ag/Ag<sup>+</sup>, possibly related to the formation and growth of corrosion products. NAB reaches stable  $E_{oc}$  values after 16 h of exposure, keeping constant close to -1.15 V vs. Ag/Ag<sup>+</sup>, suggesting the formation of a more protective layer on NAB surface. This behavior can be attributed to the Al, (5 % in Ni-Al and 11% in NAB), which can form a protective alumina layer on NAB that prevents a continuous reaction at higher temperatures.



Figure VI-4: Open circuit potential of Ni-5Al (■), NAB (◊) samples after exposure to molten carbonates at 550 °C in H<sub>2</sub>/N<sub>2</sub> atmosphere.

Figure VI-5 shows the Nyquist diagrams of Ni-5Al and NAB after exposure to molten carbonates at 550 °C and  $E=E_{OC}$ , revealing a capacitive loop at high-frequency range (HF), between 11.6 kHz and 100 Hz, and other at medium and low-frequency range (MF-LF), between 100 Hz and 11.6 mHz with a well-defined slope close to 45 °. In general, Ni-5Al has a smaller impedance response than the NAB, independently of exposure time, and its response was constant during exposure. The impedance response of NAB alloy was higher at the earlier stages, decreasing after a longer exposure time.



Figure VI-5: Nyquist diagrams of Ni-5Al (a) and NAB (b) samples after 5 days (120 h) of exposure to molten carbonates at 550 °C in an H<sub>2</sub>/N<sub>2</sub> atmosphere. Red line defines the angle of 45°.

At open circuit potential (E=E<sub>oc</sub>), the anodic reaction involves the oxidation of all alloying elements in the alloys. It is worth mentioning that H<sub>2</sub> oxidation could also occur in this system. Nitrogen reduction reaction can be involved as the cathodic reaction in an H<sub>2</sub>/N<sub>2</sub> atmosphere, possibly generating N<sub>2</sub>H<sub>4</sub> and NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> could form as reaction products.



Figure VI-6: Nyquist diagrams E=Eoc, cathodic (-30mV) and anodic (+30mV) over potential of (a) Ni5Al and (b) NAB samples after 24h of exposure to molten carbonates at 550 °C.

Figure VI-6 shows the Nyquist diagrams of Ni-5Al and NAB alloys after 24 h of exposure to molten carbonates at 550 °C at cathodic and anodic overpotentials ( $E=E_{oc}\pm 30$  mV). At HF range (11.56 kHz and 100 Hz), no significant differences are observed for Ni-5Al. Nevertheless, the impedance response of NAB alloy reveals a very well-defined capacitive loop at cathodic overpotential in this frequency domain, which was not observed at  $E=E_{oc}$  or anodic overpotential. While, at MF-LF ranges (100 Hz and 11.56

mHz), no significant differences are observed for NAB alloy, and some differences in the modulus was observed for Ni-5Al alloy. Therefore, the impedance responses at different overpotentials of both alloys suggest that the metal alloys are under mixed control in molten carbonate using an  $H_2/N_2$  atmosphere.

Figure VI-7 shows the Bode plots for both alloys during exposure to molten carbonates at 550 °C, corrected and non by the electrolyte resistance. The modulus demonstrates that the impedance response of NAB samples is one order of magnitude higher than the Ni-5Al in all frequency ranges. The corrected Bode plots of Ni-5Al and NAB samples reveal time constants superimposed, with impedance phase  $(-\theta)$  valued close to 45° at all frequency ranges, suggesting a porous electrode behavior at the HF range, associated with a film formed on the surface. Additionally, a charge transfer resistance (R<sub>ct</sub>) possibly related to the anodic reaction and double layer capacitance at the MF and LF domain, and a diffusional impedance at the LF range.

De Levie proposed  $-\theta$  close to 45 ° in the HF and 90 ° in the LF, considering that the porous electrode was composed of identical cylindrical pores [177–181], described by the following equation:

$$Z_{De \ Levie} = \sqrt{R_0 \cdot Z_0} \cdot \cot\left(l\sqrt{\frac{R_0}{Z_0}}\right) \tag{V.1}$$

Where  $Z_0 = \frac{1}{j\omega C_{dl}} \cdot \frac{1}{2\pi r}$  is the interfacial impedance ( $\Omega$  cm),  $R_0$  is the electrolyte resistance for a one-unit length pore ( $\Omega \cdot$  cm<sup>-1</sup>), given by  $R_0 = \frac{\rho}{\pi r^2}$ ,  $\rho$  is the electrolyte resistance ( $\Omega \cdot$  cm), *l* and *r* are the length and radius of pores [141]. As shown Figure VI-7, the Bode plot for Ni-5Al and NAB alloys, the - $\theta$  values are close to 45 ° at the HF. However, at the LF, the - $\theta$  values are much lower than 90 °, as De Levie described. This behavior can be related to the size and shape pore distribution [182–186] but also to dielectric properties of the film formed on the metal surfaces. This is because the MF and LF are being affected by the diffusion process and the electric double layer occurring though the film and over the surface that modified the De Levie response.



Figure VI-7: Bode plots of Ni-5Al (a) and NAB (b) samples after 6 h and 120 h of exposure to molten carbonates at 550 °C in an H<sub>2</sub>/N<sub>2</sub> atmosphere.

Figure VI-8 shows the equivalent circuit and physical model proposed for Ni-5Al and NAB alloys after exposure to molten carbonates at 550 °C. R<sub>e</sub> represents the electrolyte resistance at the electrolyte/metal interface. CPE is a constant phase element characterized by Q and  $\alpha$  parameters involving the contribution of double-layer pseudo-capacitance (C<sub>dl</sub>) [187]. R<sub>ct</sub> represents the charge transfer resistance related to the reduction reaction at the external part of the corrosion product. W represents the diffusion impedance due to the N<sub>2</sub> through the corrosion products, and Z<sub>De Levie</sub> represents a De Levie impedance related to the porosity, with parameter showed in Eq. (1).



Figure VI-8: Equivalent circuit and physical model representing (a) Ni-5Al and (b) NAB behavior exposed to molten carbonates at 550 °C in H<sub>2</sub>/N<sub>2</sub> atmosphere.

The impedance fit result of Ni-5Al and NAB alloys using the equivalent circuit proposed, is shown in Figure VI-9, whose errors  $x^2$ , varied between 1.3 and 2.1 for Ni-Al alloy and 0.4 to 2.1 for NAB alloy. The R<sub>e</sub> parameter of Ni-5Al was constant during exposure, fluctuating between 0.77 and 1.31  $\Omega \cdot \text{cm}^2$ , which were slightly lower than NAB alloy, varying between 4.86 and 7.27  $\Omega \cdot \text{cm}^2$ . Figure VI-9(b -d) shows that the R<sub>0</sub> increase for Ni-Al alloy, which extremely varied between 8.04· $\Omega$  cm<sup>2</sup> and 697.64  $\Omega \cdot \text{cm}^2$  for a longer exposure time. Instead, R<sub>0</sub> increase slightly in the NAB alloy, fluctuating between 978 and 1310  $\Omega \cdot \text{cm}^2$ , suggesting lower ion concentration in the pores, possibly due to a more substantial passivity of the film formed on the NAB surface than Ni-5Al alloy.



Figure VI-9: Pore and electrolyte resistances of Ni-5Al (a-b) and NAB (c-d) after exposure to molten carbonates at 550 °C in H<sub>2</sub>/N<sub>2</sub> atmosphere.

Figure VI-10 shows the variation of  $R_{ct}$ , for Ni-5Al varied between  $0.50 \cdot \Omega \text{ cm}^2$  and  $0.75 \ \Omega \cdot \text{cm}^2$ , while for NAB alloy significantly increasing between  $9.24 \ \Omega \cdot \text{cm}^2$  and  $179.58 \ \Omega \cdot \text{cm}^2$ . Zeng et al. [188] studied Ni and Fe-Al alloy in molten carbonates at 650 °C in air condition, reporting  $R_{ct}$  values between 10.68 and 5.35  $\Omega \cdot \text{cm}^2$  for each alloy, it means similar values for our Ni-5Al. Trinstancho-Reyes et al. reported  $R_{ct}$  for Inconel 718 alloy in Na<sub>2</sub>SO<sub>4</sub> salts at 840 °C and 580 °C in air conditions, estimating valued between 311  $\Omega \cdot \text{cm}^2$  and 193  $\Omega \cdot \text{cm}^2$  respectively [189]. Also, Pineda et al. evaluated ASTM A36 and AISI 304L in molten salts at 390 °C in air conditions, determining  $R_{ct}$  close to 118.48  $\Omega \cdot \text{cm}^2$  for carbon steel and 4770  $\Omega \cdot \text{cm}^2$  for 304L alloy [140]. Therefore, Ni-5Al and NAB alloy revealed  $R_{ct}$  values of a materials which corrosive behavior and passive materials, respectively.



Figure VI-10: Variation of charge transfer resistances of Ni-5Al (a) and NAB (b) after exposure to molten carbonates at 550 °C in H<sub>2</sub>/N<sub>2</sub> atmosphere.

The impedance fit data were used for estimating the double layer ( $C_{dl}$ ) using the Brug [187], as shown below:

$$Q = C_{dl}^{\alpha} [R_e^{-1} + R_{ct}^{-1}]^{(1-\alpha)}$$
(V.2)

When  $R_{ct}$  is much higher than  $R_e$ , the inverse  $R_{ct}$  is negligible over the inverse of  $R_e$ , obtaining the simplified, as shown in the following equation:

$$C_{dl} = R_e^{(1-\alpha)/\alpha} Q^{1/\alpha} \tag{V.3}$$

Figure VI-11 shows the variation of  $C_{dl}$  of Ni-5Al and NAB alloys after exposure to molten carbonates, revealing those values between  $1.64 \cdot 10^{-3}$  and  $2.43 \cdot 10^{-6} \,\mu\text{F} \,\text{cm}^2$  for Ni-5Al and lower values  $1.10 \cdot 10^{-4}$  until  $4.42 \cdot 10^6 \,\mu\text{F} \,\text{cm}^2$  for NAB alloy. Zeng et al. [188], Tristancho-Reyes et al. [189], and Pineda et al. [140] reported  $C_{dl}$  values for Ni alloy, Fe-Al alloy, Inconel 718 alloy, and AISI 304L alloy, wich values are similar to Ni-5Al alloy. Zeng et al. [188] reported an increase of  $C_{dl}$  between  $2.11 \cdot 10^{-3}$  to  $1.21 \cdot 10^{-2} \,\text{F} \,\text{cm}^{-2}$  for Ni alloy after 62 h of exposure and a lower variation for Fe-Al alloy, almost  $2.41 \cdot 10^{-4} \,\text{Fcm}^{-2}$  after 74 h of exposure. Trinstancho-Reyes et al. [189] reported a  $C_{dl}$  of  $9 \cdot 10^{-3} \,\text{F}$  for

Inconel 718 alloy at 840 °C and  $4.4 \cdot 10^{-2}$  F for 580 °C. Pineda et al. [140] estimated C<sub>dl</sub> values near  $1.22 \cdot 10^{-2}$  F cm<sup>2</sup> for AISI 304L after 21 days of exposure. Therefore, Ni-5Al alloy has higher values than NAB alloy, showing a more significant variation during the exposure. It should be noted that the C<sub>dl</sub> values of Ni-5Al are similar to those of other Ni-based alloys, Fe-Al alloys, Inconel 718, and AISI 304L. The C<sub>dl</sub> values remain constant for NAB alloy. Pineda et al. [140] proposed that this behavior can be related to an improvement in the corrosion resistance.



Figure VI-11: Double layer capacitance of Ni-5Al (a) and NAB alloy (b), both samples after exposure to molten carbonates at 550 °C.

### 6.3.4 Microhardness

Before exposure, microhardness tests for Ni-5Al and NAB alloys revealed a value close to  $169 \pm 27$  HV and  $316 \pm 27$  HV, respectively. After 120 h of exposure, the microhardness increased for Ni-5Al until  $212 \pm 15$  HV, and the NAB alloy was kept constant  $324 \pm 30$  HV, possibly due to the effect of the nature of corrosion products formed on each alloy [190]. On the other hand, some authors, such as Kodentsov et al. [53], reported an increase in the microhardness of Ni-based alloys due to the nitridization, which process occurs at specific conditions of temperature and pressure of N<sub>2</sub>, which could be a possibility for the increase of microhardness in Ni-5Al alloy. However, Yang and Wu [191] studied a Ni-Al alloyed layer after heat treatment, which discovered that at  $400^{\circ}$ C the highest microhardness, 430 HV, occurred due to the re-crystallization of intermetallic nickel aluminide.

### 6.4 Conclusions

This work focuses on the corrosion of a nickel-aluminum and a nickel-aluminum bronze after exposure to molten carbonate at high temperatures. Both alloys were manufactured by laser powder bed fusion. The main results revealed:

• A higher microhardness was determined for NAB alloy compared to Ni-5Al, associated to the alloying elements and intermetallic compounds of the first.

However, the microhardness increased on Ni-5Al after exposure due to the recrystallization at high-temperature exposure and the incorporation of  $N_2$  in the surface.

• The corrosion products formed on Ni-5Al and NAB alloys were composed of deposits from the electrolyte but also of oxide layers with different chemical compositions. The oxide film was formed mainly of NiOOH layer for Ni-5Al alloy and Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O for NAB alloy.

The impedance analysis revealed that both alloys had similar behavior but what was occurring on the surface differed. It was attributed to the film formed on the surface, which in the NAB demonstrates being more protective compared to the Ni-5Al.

# VII. CHAPTER IV: SUITABILITY OF NICKEL ALUMINIUM BRONZE ALLOY FABRICATED BY LASER POWDER BED FUSION TO BE USED IN THE MARINE ENVIRONMENT

### 7.1 Introduction

Marine structures such as ships, docks, and oil/gas plants are made from different metal alloys based on ferrous and non-ferrous elements. The ship infrastructures are mainly made of steel and aluminium alloys and, some functional parts can be made of copper alloys, such as bronze and brass. Although these copper alloys have exceptional mechanical, corrosion, and antifouling properties, they are often used for functional parts and hull sheathing for small fishing vessels due to their high price compared to ferrous alloys. Figure VII-1 shows a radar chart that compares the price, mechanical, and corrosion properties of different materials used in marine environments. As observed, the Ni alloys present the highest elongation and strength. However, they are also the most expensive on the list. Regarding corrosion rate, all alloys, except for steel, demonstrate low corrosion rate in seawater (0.03-0.003 mm  $\cdot$  y<sup>-1</sup>). This is attributed to their ability to form a protective passive layer, shielding the rest of the material from corrosion.

Cu-11Al-5Ni-4Fe wt% alloy is also known as NAB (nickel aluminium bronze) alloy, which has been researched in-depth due to its high strength, good impact toughness, damping capacity, good corrosion resistance, wear resistance, and non-sparking [192]. This makes it a candidate for aerospace, architecture, marine defence, commercial offshore oil/gas and petrochemical, desalination, and water condenser systems industries [90]. NAB's naval applications are focused on piping, valves, fittings, heat exchangers, propellers, sealing flanges, sonar equipment, flexible couplings, and periscope assemblies [192]. Cu-11Al-5Ni-4Fe wt% alloy is essential to submarines [193] since it can suppress sound for silent operations due to its good anti-damping properties, which are twice that of steel [90].

NAB alloy has been fabricated principally by continuous and centrifugal casting, which allows it to achieve different forms. Then, it can be processed in hot by extrusion, rolling, and forging to obtain the alloy in its wrought working form [90]. The tensile strength in the cast and wrought forms (ASTM denomination C958xx and UNS C63xxx, respectively) differ slightly (600 – 760 MPa and 621-760 MPa), whereas, the elongation properties have been demonstrated to be in the same range. Also, the alloy has been indicated as a great candidate for pumps and valves due to its high corrosion and wear resistance. Thus, it does not need to be coated [194]. However, due to advancements in modern manufacturing methods, there is currently insufficient information to confidently determine if the alloy is more prone to corrosion when produced using additive manufacturing (AM).

Different alloys fabricated by additive manufacturing have been exposed to corrosive environments to observe their evolution. M. Bajt et al. [195] studied the Ti-6Al-4V alloy

in its wrought form and those fabricated through laser powder bed fusion (LPBF) after exposure to artificial saliva. They observed that the most important factor that triggers the corrosion process was the crystallographic phases present in the alloy, which, consequently, is influenced by the fabrication method. A. Racot et al. [196] exposed the 316L (stainless steel) to 4 mol·1<sup>-1</sup> of NaCl at 50 °C obtained as wrought and fabricated by LPBF. They stated that the grain shape is the key factor in determining corrosion, as the oxide layer forms at the grain boundaries, offering passivation and protection to the rest of the material. This phenomenon has also been observed in other studies on passive materials, indicating that the grain size and its shape uniformity play a crucial role in determining the quality of the passive layer against corrosion [197,198]. Hence, it could also be inferred that a longer grain, like the columnar grain achieved via additive manufacturing, may not offer adequate oxidation to the surface coverage. Consequently, diminishing the protective behaviour of the passive layer.

NAB alloy was studied on its as-cast and as-built condition (obtained from electron beam melting) exposed to a 3.5 wt% NaCl solution [199]. The authors found that both as-cast and as-built samples showed selective phase corrosion, specifically of the martensite ( $\beta$ ') and the intermetallic (NiAl). C. Xu et al. [200] studied the NAB exposed to 3.5 wt% NaCl in as-cast and built conditions (fabricated through wire arc additive manufacturing). They conclude that the improvement in corrosion resistance of as-built samples is due to the absence of the martensitic phase, which is often selectively corroded, and the uniform distribution of Al<sub>2</sub>O<sub>3</sub> formed in these samples after the immersion process. Since the corrosion performance of the alloy can be determined by the microstructure, several studies have been carried out to explain the better NAB microstructure under different heat treatments and surface modifications [89,201,202].



Figure VII-1: Radar chart used to compare different alloys used in marine environments. The data were collected from diverse references [90,203–206].
Given the significance of phase composition in determining corrosion behaviour, this study aims to assess the corrosion behaviour of samples manufactured using the LPBF technique, both with and without heat treatment. The novelty lies in enhancing the understanding of the oxidation progression of these components when exposed to a solution mimicking seawater salt content. For that, built samples with and without heat treatment are immersed into 3.5 wt% NaCl for 30 days. Corrosion performance is evaluated by electrochemical techniques, such as electrochemical impedance spectroscopy and polarization curves. The surface by X-ray photoelectron spectroscopy (XPS) before and after exposure.

## 7.2 Methodology

#### 7.2.1 Sample fabrication

Cu-11Al-5Ni-4Fe wt% alloyed powder (<40  $\mu$ m, CNPC powder group CO) was used to manufacture bulk samples using the LPBF technique (GE - Concept Laser Mlab using 200R machine). The process parameters were 30  $\mu$ m and 80  $\mu$ m for the layer thickness and hatch space, while the laser power and scanning speed were kept at 180 W and 600 mm·s<sup>-1</sup>, with a total volumetric energy density (VED) of 125 J·mm<sup>-3</sup>. Each sample was fabricated with a cylindrical shape of 6 mm and 8 mm in length and diameter, respectively, constructed over a 100 x 100 mm copper platform. After fabrication, pieces were removed from the Cu platform using wire electrical discharge machining (W-EDM). After fabrication, two different heat treatments were used to create two sets of samples: one underwent quenching and tempering (Q+T), while the other underwent annealing (A). Figure VII-2 provides a schematic representation of the heat treatment processes. Regarding the quenching and tempering process, the samples were heated to 900 °C for 1 h, rapidly cooled in water, and then heated to 700 °C for 5 h. Finally, they were cooled in the air. For the annealing process, the samples were heated to 900 °C for 2 h, followed by furnace cooling [89,90].

Before exposure to the electrolyte, the samples underwent a grinding process using grit sandpaper ranging from #400 to #4000, followed by polishing with colloidal silica suspension.



Figure VII-2: Schematic representation of each heat treatment, where "Q+T" is the quenching and tempering and "A" is annealing.

# 7.2.2 Sample characterization

Morphologic surface images were obtained through field emission-scanning electron microscope (FE-SEM) QUANTA FEG 250. In contrast, the surface chemistry was analyzed by X-ray Photoelectron Spectroscopy (XPS), employing a K-alpha photoelectron spectrometer (Thermo Scientific). The alloy phases were characterized by X-ray diffraction (XRD) using Rigaku equipment (MiniFlex 600, detector D/tex Ultra 2 High-Speed 1D), equipped with Cu K $\alpha$ 1 radiation source ( $\lambda$  =1.54056 Å) using a scan rate of  $0.02^{\circ} \cdot s^{-1}$ .

### 7.2.3 Electrochemical measurements

The electrochemical measurements were carried out using a potentiostat/galvanostat (Bio-Logic, VSP) and a three-electrode electrochemical cell, with a Pt grid and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. NAB samples were utilized as the working electrode with a geometrical area of 0.28 cm<sup>2</sup>, which were immersed for 30 days in 3.5 wt% NaCl solution at room temperature. Chronopotentiometry at open circuit was performed for 1 h, and then electrochemical impedance spectroscopy (EIS) was measured after 1, 3, 7, 14, 21, and 30 days. EIS was conducted in duplicated between 65 kHz to 3 mHz with seven points per decade and using an amplitude of 10 mV at  $E = E_{OC}$ . In parallel, different samples were tested by impedance spectroscopy at different overpotentials (cathodic and anodic)  $E_c=E_{OC}$  -200 mV and  $E_a=E_{OC}+200$  mV after 30 days of exposure. Linear sweep voltammetry (LSV) was performed at  $E = E_{OC} \pm 200$  mV vs. SCE using a sweep rate of 0.1 mV·s<sup>-1</sup> after 30 days of exposure.

# 7.3 Results

#### 7.3.1 Microstructure characterization

Figure VII-3 shows the micrographs obtained by FE-SEM of the sample surfaces before and after 30 days of exposure to 3.5 wt% NaCl solution at room temperature. Figure VII-3 (a) shows the AB sample before exposure, which has a homogeneous surface with some pores and defects produced by the AM process. Figure VII-3 (b-c) depicts the heat-treated samples before exposure, revealing the presence of intermetallic compounds that emerged during the heating process. This phenomenon is attributed to the alloy's homogenization, facilitating the formation of stable phases. Figure VII-3 (d-f) shows the AB, quenching plus tempering (Q+T), and annealed (A) samples after exposure. They exhibit a rough surface with some salt-covered pores.



Figure VII-3: FESEM micrograph (a-c) before and (d-f) after 30 days of exposure to 3.5 wt% NaCl solution at 23 °C for (a,d) as-built (b,e) quenching + tempering and (c,f) annealed samples.

Figure VII-4 shows the XRD results for A, Q+T, and AB samples before exposure. The samples are constituted of the same phases, such as the  $\alpha$ -cubic phase, which consists mainly of copper,  $\beta$ ' phase representing martensite, ordered as 3R or 2H, is formed through rapid cooling during manufacturing processes, and the  $\kappa$ -phase (Kappa phase), which comprises intermetallic combinations of various alloying elements. The  $\kappa$ -phase includes Fe-rich components,  $\kappa_I$  and  $\kappa_{II}$  are based on Fe<sub>3</sub>Al/FeAl (DO<sub>3</sub> or B2) [104,207], and  $\kappa_{IV}$  is Ni-rich based on NiAl (B2) [104,124,208–210]. Furthermore, the stable  $\beta$  phase (BCC) is often masked by the  $\alpha$  phase due to their cubic structures and similar interplanar spacings. As a result, they diffract at equivalent angles, making it challenging to distinguish between them in the analysis [211]. The AB sample exhibits a more rugged spectrum compared to the others, attributed to its fabrication method. Instead, the heat-treated samples demonstrated diffraction at accurate angles due to the elevated temperature, which promoted stress relief and alloy homogenization.

The XRD pattern of Q+T showed  $\alpha$  and  $\kappa$  phases and a small quantity of  $\beta$ ', which is a product of the quenching and then their stabilization as  $\beta$  due to tempering [89,212]. In contrast, the XRD pattern of the A sample revealed a higher presence of  $\kappa$  phases. This can be attributed to the prolonged exposure time at high temperatures, facilitating their appearance and stabilization.



Figure VII-4: XRD pattern for A, Q+T, and AB samples before exposure.

## 7.3.2 Electrochemical behaviour

Figure VII-5 shows the open circuit potential ( $E_{OC}$ ) variation towards more anodic potentials, being more drastic in the AB sample. The  $E_{OC}$  varied with exposure time, reaching their stability near -180 mV and -200 mV for all samples between 14 and 21 days of exposure. Additionally, the heat-treated samples show very similar behaviour, being more constant with exposure time, suggesting the formation of a stable corrosion product on the surface.



Figure VII-5: Open circuit potential (E<sub>OC</sub>) result of A, Q+T, and AB samples after exposure to 3.5 wt% NaCl with exposure time.

Figure VII-6 shows the EIS results through Nyquist plots and Bode diagrams of A, Q+T, and AB samples after 1 and 30 days of exposure at room temperature at  $E=E_{OC}$ . As observed, for all samples, the impedance response demonstrates two-time constants at high and low frequencies (HF and LF), which can be identified clearly for A and Q+T samples. However, the capacitive loops are superposed for the AB sample at the beginning, as shown in the phase diagram after 1 day of exposure, exhibiting a wider signal between  $10^{-1}$  Hz and  $10^{3}$  Hz. AB sample shows a more significant resistance than the heat-treated samples after shorter and longer exposure times, revealing two-time constants.



Figure VII-6: Nyquist plot and Bode diagrams after (a,c,e) 1 and (b,d,f) 30 days of exposure to 3.5 wt% NaCl solution at 23 °C. (a-b) Nyquist plots, (c-d) phases and (e-f) modulus not corrected by the electrolyte resistance.

Figure VII-7 shows the LSV curves and the cathodic and anodic current densities at different overpotentials ( $\eta$ ) for all samples collected after 30 days of exposure to 3.5 wt% NaCl at room temperature. As mentioned, the mixed potential of the AB sample is shifted to more anodic potential compared to the heat-treated samples. The cathodic current density (i<sub>c</sub>) of the AB sample, associated with the diffusion-controlled region, is kept lower than the heat-treated samples, reaching a quasi-steady state near 1.9 x 10<sup>-5</sup> A·cm<sup>-2</sup>. However, the anodic current density (i<sub>a</sub>) increases quickly with the anodic  $\eta$ , and this effect is more pronounced for the AB sample. In fact, the AB sample even surpasses the other samples at around  $\eta$ =100 mV, indicating that it is more significantly influenced by anodic overpotentials. This latter feature could be related to the break of an oxide layer formed on the metal samples.



Figure VII-7: (a) LSV curve of NAB alloy after 30 days of exposure to 3.5 wt% NaCl at room temperature collected at a scan rate of 0.1 mV·s<sup>-1</sup>. Variation of (b) cathodic and (c) anodic current densities as a function of overpotentials.

## 7.3.3 Surface composition

Figure VII-8 shows the XPS spectra of all samples before and after 30 days of exposure to 3.5 wt% NaCl. After 30 days, new signals were detected in the samples, as those associated with Fe (Fe 3p and Fe 2s), and variation in the relative amount of these elements. Additionally, the oxygen exhibited to be predominant after exposure, surpassing the quantities of the alloying elements. Indeed, Figure VII-8 (a) shows the XPS before exposure, which reveals the presence of Cu and alloying elements, such as Al and Fe. In addition, Figure VII-8 (b) shows the XPS after exposure, which exhibits all the alloying elements, including Ni, and also the contribution of Cl, possibly forming a CuCl or CuCl<sub>2</sub>, as reported previously [200,213,214].



Figure VII-8: XPS spectra of all samples (a) before and (b) after 30 days of exposure to 3.5 wt% NaCl at room temperature.

Figure VII-9 shows the relative quantity of some alloying elements, oxygen, and chloride content before and after exposure. Fe content exhibits a relatively small variation, ranging from 2 % to 6 %, despite its low initial concentration in the alloy. This is likely attributed to the formation of intermetallic phases (Fe-rich). TheAl was present in all heat-treated samples before and after exposure due to the temperature promoting the surface oxidation and precipitation of intermetallic, such as NiAl and FeAl over the surface. Instead, Ni was present in each heat-treated sample in a very low amount, and for this reason, was not added to the graph. Oxygen content varied from 40 % to 62 %, which decreased after exposure, possibly due to the presence of chloride and the increase of certain alloying elements, like Al and Fe, which shielded the oxygen signal.



Figure V-9: The relative quantity of elements processed from XPS spectra before and after exposure for each sample.

#### 7.4 Discussion

#### 7.4.1 Electrochemical analysis

Figure VII-10 shows the impedance spectroscopy performed at  $E_c=E_{OC}$  -200 mV (cathodic) and  $E_a=E_{OC}+200$  mV (anodic) after 30 days of exposure. This was carried out to understand the origin of the two-time constants and to know how the anodic or cathodic reactions influence the system. Figure VII-10 (a) shows the EIS performed at overpotentials and Figure VII-10 (b) performed at  $E=E_{OC}$ . It is established that both the cathodic and anodic reactions are involved in the process, and by principle at  $E=E_{OC}$  they should occur at the same rate. However, the impedance response obtained at cathodic potentials is higher than the anodic, suggesting that the oxygen reduction reaction (ORR) can significantly influence the impedance response. This observation is consistent with the finding from the limiting density current in the LSV curve at cathodic overpotentials. The anodic eq. (VII.1) and cathodic reactions eq. (VII.3) involved are [213]:

$$Cu + Cl^{-} \leftrightarrow CuCl + e^{-}$$
 (VII.1)

Then, CuCl, due to its instability [215], reacts with Cl<sup>-</sup> as:

$$CuCl + Cl^{-} \leftrightarrow CuCl_{2}^{-} \tag{VII.2}$$

Next, the  $CuCl_2$  can react to form the  $Cu_2O$  as shown in eq. (VI.3)

$$2CuCl_2 + 2OH \rightarrow Cu_2O + H_2O + 4Cl^{-}$$
(VII.3)

In this system, the anodic current is attributed to the metal dissolution, which contributes less to the impedance response collected at  $E_{OC}$ . At the same time, the cathodic reaction can be related to oxygen reduction, which is also controlled by mass transport and can occur as follows:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (VI.4)$$

The cathodic impedance can be depicted as a double-layer capacitance ( $C_{dl}$ ) in parallel with a charge transfer resistance ( $R_{ct}$ ), connected in series with an impedance related to the O<sub>2</sub> mass transport ( $Z_{wc}$ ). Regarding the double-layer capacitance, it often presents a distribution of reactivity, which is expressed in the impedance response as depressed semicircles, which could be better represented by constant phase element (CPE), expressed in terms of Q and  $\alpha$  [213]. Figure VII-10 shows the equivalent circuit proposed to be applied in the whole frequency range (65 kHz to 0.04 Hz), which is composed of a constant phase element (representing the double-layer capacitance, CPE<sub>dl</sub>) in parallel to the R<sub>ct</sub>, and in series to the Warburg impedance ( $W_c$ ), representing the O<sub>2</sub> mass transport. Table VII-1 summarizes the impedance parameters obtained from the fitted results. The values indicate that the loops at high frequency (HF) are related to the double-layer

capacitance, since the C<sub>dl</sub> estimated by the Brug formula [213], exhibit values of doublelayer capacitance (10-40  $\mu$ F·cm<sup>-2</sup>) in parallel to the charge transfer resistance. Thus, the loop at lower frequency (LF) corresponds to O<sub>2</sub> mass transport, where the Warburg coefficient (k<sub>c</sub>) was estimated by the expression:

$$Z_{Wc} = \frac{1}{k_c \sqrt{j\omega}} \tag{VI.5}$$



Figure VII-10: Nyquist plot of AB samples after 30 days of exposure to 3.5 wt% NaCl performed at (a)  $E_c=E_{OC}-200 \text{ mV}$  and  $E_a=E_{OC}+200 \text{ mV}$  and (b) open circuit potential ( $E_{OC}$ ).

Figure VII-11 also shows a scheme of the surface oxide evolution of AB and heat-treated samples. The EIS parameters indicate that the contribution of mass transport in heat-treated samples is higher than for the AB samples at any time, suggesting that their oxide is more irregular with small channels.

In all conditions, NAB alloy presents a thin oxide layer composed mainly of copper oxide at the beginning. It was evidenced by XPS surface analysis, which demonstrates that the surface is composed primarily of copper, while the heat-treated samples show the presence of the other alloying elements due to the stabilization of intermetallic phases. It should be noted that Cu oxide is a semiconductor and, therefore, hard to detect by EIS. After exposure, these intermetallic phases play an important role in surface oxidation due to the contact with the electrolytes. AB samples are oxidized more uniformly, while in the heat-treated samples, the oxide could grow on those sites intermetallic-free. The latter provokes an oxide with more tortuosity than the AB sample. EIS analysis revealed that the AB sample shows a higher resistance than the other samples with less apparent oxide thickness. It should be noted that after 1 day of exposure, AB exhibited two capacitive loops overlapped, evidenced by the wider signal by the phase diagram, which indicates that the oxide from the beginning was more homogeneous or less tortuous than the heat-treated samples. However, after the exposure time, the oxide grew and became similar to the others. Several authors have studied the influence of different types of intermetallic on corrosion performance, reaching an agreement that depends on the intermetallic and the metal matrix to define if they could have a negative influence [216,217]. It is known that intermetallic can have different potentials to the metal matrix, which can be considered as a cathodic or anodic site, favouring the formation of micro-galvanic cells [217], and the dealloying of the alloy around the intermetallic or the intermetallic itself. In this system, the intermetallic, rich in Fe and Ni, can act as cathodic sites. Therefore, produce the dealloying of the surrounding area.



Figure VII-11: schematic representation of the oxide evolution and the equivalent circuit.

Additionally, the polarization curves suggest that the alloy oxidation occurs quickly on the heat-treated samples at the beginning, showing a semi-plateau similar to some passive materials [181]. While on the AB samples, the anodic current density increases faster but with lower current density, which could be attributed to a variation in the real electroactive area during the oxidation of the metal surface.

ID	Time / days		Estimated by Brug					
		$ m R_{e}$ / $\Omega\cdot cm^2$	$\frac{Q_{dl} \times 10^{-4} /}{F \cdot cm^{-2} \cdot s^{(\alpha-1)}}$	-αd1/-	$k_c \times 10^{-4} / s^{0.5} \cdot \Omega^{-1} \cdot cm^{-2}$	$\frac{R_{ct} \times 10^{3}}{\Omega \cdot cm^{2}}$	$\chi^2$	C <sub>dl</sub> / µF∙cm <sup>-2</sup>
AB	1	$11.5 \pm 0.5$	$1.6 \pm 0.5$	$0.7 \pm 0.0$	$9.0 \pm 1.2$	$3.4 \pm 1.5$	1.1	8.5
	14	$15.8\pm0.6$	$0.5 \pm 0.1$	$0.7 \pm 0.1$	7.2±1.2	$0.7 \pm 0.1$	2.1	3.3
	30	$10.9\pm1.4$	$0.4 \pm 0.1$	$0.7 \pm 0.1$	$6.8 \pm 0.2$	$0.6 \pm 0.2$	1.6	2.3
Q+T	1	$9.1 \pm 0.1$	$3.0 \pm 1.0$	$0.6 \pm 0.1$	$14.3 \pm 4.0$	$0.4 \pm 0.2$	3.3	10.3
	14	$13.3 \pm 3.8$	$1.8 \pm 0.4$	$0.7 \pm 0.1$	$20.9 \pm 0.2$	$1.8 \pm 0.0$	1.8	32.2
	30	$12.8 \pm 2.6$	$5.7 \pm 3.0$	$0.6 \pm 0.1$	$24.5 \pm 8.9$	$0.6 \pm 0.1$	2.5	32.1
А	1	$10.1 \pm 1.1$	$1.8 \pm 0.2$	$0.7 \pm 0.1$	$26.9\pm10.8$	$0.5 \pm 0.3$	2.3	17.6
	14	$12.5 \pm 2.3$	$2.5 \pm 0.9$	$0.7 \pm 0.0$	$20.0 \pm 3.5$	$0.4 \pm 0.0$	2.7	20.7
	30	$14.0 \pm 3.6$	$5.3 \pm 2.1$	$0.7 \pm 0.1$	$29.8 \pm 3.2$	$0.9 \pm 0.2$	1.7	42.5

Table VII-1: Summary of the EIS parameters in the frequency range of 0.04 Hz to 11.3 kHz.

# 7.4.2 Suitability of additive manufacturing to produce pieces with better corrosion performance

Fabrication of pieces based on the LPBF technique leaves some internal defects in the material compared to other production methods. Examples are porosity, residual stress [218], columnar grains in the building direction, which conduce to a crystalline texture due to the rapid solidification [219], non-equilibrium phase formation, and other types of intermetallic. The AB sample shows a greater presence of  $\beta$ ' (martensite) phase, which is signalled responsible for the preferential dissolution in a corrosive environment [89,220]. However, other studies have indicated that microgalvanic couple formation between an intermetallic, such as Fe-Al ( $\kappa_{II}$ ), as well as the  $\beta$ -phase, are corroded preferentially over the  $\alpha$ -phase matrix [212,221]. Therefore, the microstructural factor is relevant to understanding the dealloying or preferential corrosion mechanism.

The thermally treated samples produce changes in the microstructure originally obtained by LPBF. According to XRD patterns, Q+T and A samples had mainly grains of  $\beta$ ' and  $\alpha$ -phase in earlier stages, to having later more  $\beta$  and  $\kappa$  type -phases. This caused a porous oxide formation on the surface since the intermetallic can behave as cathodic sites regarding the matrix. In other words, the intermetallic presence favours the porosity and tortuosity in the film, which contributes to a decrease in alloy protection. Several studies were revised to understand the phenomenon better, as shown in Table VII-2.

A 11	Fabrication	Exposure	i <sub>corr</sub>	E <sub>corr</sub> vs. SCE	$ \mathbf{Z}_{\mathrm{LF}} $	Ref	
Alloy	method	time / h	$/ \mu A \cdot cm^{-2}$	/ mV	$/ \Omega \cdot cm^2$		
NAB	LPBF		0.6	170	8 106		
	LPBF + Q+T	720	0.0	-170	0,190 2 785	**	
	LPBF		1.1	-223	2,765		
	+annealed		1.2	-240	2,301		
	LPBF	1	6.5	-265	-		
NAB	Cast		3.0	-275	-	[222]	
	Wrought		4.0	-264	-		
NAB	EBM	168	0.6	~-280	~10,500	[100]	
INAD	Cast		1.8	~-280	~9,500	[177]	
NAB	WAAM	48	$14.9 \pm 14.4$	$-0.26\pm0.02$	~4,382	[200]	
	Cast		$16.2\pm4.0$	-0.27±0.01	~3,982	[200]	
NAB	Cast						
	Cast +		7.0	-259	~20,000	[220]	
	annealed	720	7.5	-261	~10,500		
	Cast +		6.2	-278	~20,000		
	quenched						
NAB	Cast	480	1.5	-289	~3,935	[214]	
NAB	Cast	1	2.5	-305	~1,972	[223]	
	Cast	720	1.6	250	. 18 083	[201]	
NAB	Cast + laser		1.0	-230	~16,065		
	treatment		0.2	-300	~40,141		
NAB	Cast	480	0.8	-226	~64,845	[224]	
NAB	Cast	1	6.8	-277	-	[225]	
NAB	Cast	720					
	Cast +		1.4	-262	~15,620	[89]	
	annealed		3.2	-291	~10,770		
	Cast +		0.2	-284	~70,710		
	quenched						
NAB	Cast	2	~6.3	~-290	-	) [226]	
	Casi	12	-	-	~28,440		
NAB	Cast	72	9	-298±5	~3,350	[227]	
	Cast	0.27	17	-262	~2 110		
NAB	Cast +		0.9	-202	~2,110	[228]	
	annealed		0.9	-233	-2,550		

Table VII-2: Comparison of electrochemical parameters extracted from different articles that studied the NAB alloy exposed to 3.5 % NaCl.

\*\* Obtained from the present work

Table VII-2 compares electrochemical parameters obtained from the literature review for NAB exposed to 3.5 wt% NaCl for different exposure times and fabrication methods, revealing the effect of the fabrication methods and heat treatment. As is observed, almost all samples fabricated through additive manufacturing, such as LPBF, electron beam

melting (EBM), and wire arc additive manufacturing (WAAM), show corrosion current densities (i) lower compared to their counterparts i.e., those obtained by the conventional method. W. Zhai et al. [199] attribute the lower icorr in samples manufactured by EBM compared to the cast ones to the phase preferential dissolution of certain phases. Specifically, in the first group, the affected phase was the NiAl ( $\kappa$ -phase), whereas in the other, it was the  $\beta$ ' phase, along with the eutectoid structure ( $\alpha + \kappa_{III}$ ). C. Xu et al. [200] assigned that the WAAM samples demonstrated low i due to the finer and discontinued  $\kappa_{III}$  (Ni-rich) would be effective in avoiding electrolyte inlet to the corrosion film. The samples heat treated by annealing show a greater icorr and a lower impedance modulus (|Z<sub>LF</sub>|) due principally to the stabilization and proliferation of the intermetallic compounds [89,220], which can cause the dealloying of the surrounding area or corrode itself. The  $|Z_{LF}|$  obtained in this work was also lower for heat-treated samples compared to the AB. which can be attributed to the presence of an oxide layer partially covering the surface of the former. It should be noted that Table VII-2 shows a correlation between current density and the impedance modulus at low frequency, which is a great non-destructive method to intuit the tendency of alloy resistance to the exposed medium.

Therefore, the manufacturing method and the heat treatment are essential to producing pieces of NAB and understanding the corrosion mechanism. The first advantage of material production by AM is the rapid solidification, which avoids the formation of the equilibrium phases. This favours uniform oxide formation, which blocks oxygen diffusion and, thus, improves corrosion protection. The second advantage is that it does not require a post-heat treatment to enhance the corrosion performance, which means energy and time-saving.

# 7.5 Conclusions

The NAB alloy used in marine environments manufactured by LPBF was tested before and after exposure to a 3.5 wt% NaCl solution with and without heat treatment by electrochemical and complementary techniques. The main conclusions are summarized below.

• The alloy in condition AB responds better to corrosion than its heat-treated counterpart because the temperature causes a phase transformation that increases the intermetallic phases, sites where the oxide layer does not develop. Thus, the oxide evolves with small channels which allow the electrolyte to pass. In this way, the treated sample surfaces are partially covered and protected, while AB samples have a more homogeneous oxide layer.

• Impedance spectroscopy analysis reveals that the oxygen reduction reaction plays a substantial role in the impedance response. The observed loops in the impedance spectra are associated with both the double-layer capacitance and the mass transport of oxygen, occurring at high and low frequencies, respectively. Conversely, the contribution of the anodic reaction, primarily attributed to metallic dissolution, has a relatively minor impact on the overall impedance.

• Parts manufactured using AM of the NAB alloy can then be used directly after its manufacture, that is to say, without requiring a subsequent treatment, since their properties against corrosion are demonstrated to be maximized.

# VIII. GENERAL CONCLUSION

Therefore, is it possible to indicate that the general conclusion regarding the hypothesis was partially confirmed because adding Cu to Ni-Al alloys enhanced the corrosion resistance in molten carbonate, which is determined by the morphology and chemical composition of the oxide film formed on Cu-Ni-Al alloy. However, incorporating CeO<sub>2</sub>-NPs into Cu-50Ni-5Al alloys increased the microhardness and corrosion resistance. Meanwhile, it is suggested to continue researching different percentages of nanoparticle addition and the impact on catalytic properties.

In Chapter I was studying Cu-11Al-5Ni-4Fe (NAB alloy), manufactured by Laser Powder Bed Fusion (LPBF). The effect of annealing heat treatment on the porosity, mechanical, and corrosion properties was analyzed. The mechanical tests revealed that the porosity directly affects the micro-hardness. In addition, a martensite phase transformation to  $\alpha$ phase was found with heat treatment, determining that the annealing creates a passive layer of Al under the surface, which improves the corrosion resistance. The samples were exposed to molten carbonates in an aerated atmosphere. The gravimetric results established that the pores affected the corrosion resistance. Therefore, the morphological and the micro-macrostructural characterization were achieved, corresponding to the specific objectives 1 and 2. However, it is necessary to continue studying how arbitrary geometry would affect it.

Chapter II studied the effect of CeO<sub>2</sub> nanoparticles (CeO<sub>2</sub>–NPs) in Cu-Ni-Al alloy at high temperatures. These samples were manufactured by spark plasma sintering (SPS) and analyzed using microstructural, mechanical, electrochemical, and surface analyses before and after exposure to the molten carbonates at 550 °C in an aerated atmosphere, promoting corrosion products over the surfaces, which were modified with nanoparticles incorporated (0,1,3, and 5 wt.%). The samples that showed better mechanical behavior showed an increase on microhardness and higher corrosion resistance due to a bigger impedance module. Therefore, Cu–50Ni–5Al + 1 wt.% CeO<sub>2</sub>–NPs, have a promissory use at high temperatures, achieved specific objectives 1 and 2. However, it is considered important to continue impedance studies to determine whether the increase in the addition of nanoparticles is directly related to the corrosion resistance of the alloys.

Chapter III compared Ni-5Al (commercial alloy) and Cu-11Al-5Ni-4Fe (NAB alloy) manufactured by Laser Powder Bed Fusion (LPBF), exposed to molten carbonates in a controlled atmosphere (H<sub>2</sub>/N<sub>2</sub>) at 550°C for 5 days, formed an oxide film over the surface for both alloys, mainly of NiOOH for Ni-5Al and Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O for NAB alloy. According to the literature, NiOOH is associated with excellent catalytic properties. Also, the impedance analysis revealed that both alloys had similar behavior but what was occurring on the surface differed. It was attributed to the film formed on the surface, which in the NAB demonstrates being more protective than the Ni-5Al.

Due to the excellent corrosion resistance properties that Cu-11Al-5Ni-4Fe (NAB alloy) shows at high temperatures, a study was carried out in Chapter IV in a marine environment of the alloy manufactured by laser powder bed fusion (LPBF), which corresponds to Chapter IV. Therefore, chemical, microstructural, and electrochemical measurements were carried out in an aerated NaCl solution. It was concluded that the NAB alloy has excellent corrosion resistance manufactured by LPBF, compared to other alloys used in container ships.

Finally, it can be concluded that NAB alloy has excellent corrosion resistance at high temperatures compared to the commercial alloy Ni-5Al. Therefore, it is suggested that the study of its catalytic behavior be continued to verify its possible use as an electrode. Also, it is suggested to analyze the influence of CeO<sub>2</sub>-NPs on the electrochemical behavior of Cu-Ni-Al alloys exposed to molten carbonate, using different concentrations and manufactured methods because the only manufacturing methodology that could effectively generate arbitrary porosity is LPBF. Due to the excellent corrosion resistance shown by the NAB alloy, it is suggested to continue to research its behavior in different molten salts at high temperatures for new applications in the energy sector as material for containers or pipes that transport molten salts.

#### REFERENCES

- 1. Ahmad, T.; Zhang, D. A Critical Review of Comparative Global Historical Energy Consumption and Future Demand: The Story Told so Far. *Energy Reports* **2020**, *6*, 1973–1991, doi:10.1016/j.egyr.2020.07.020.
- 2. Cook, M. Trends in Global Energy Supply and Demand. *Developments in Petroleum Science* 2021, 71, 15–42, doi:10.1016/B978-0-12-821190-8.00002-2.
- 3. Jamshidi, M.; Askarzadeh, A. Techno-Economic Analysis and Size Optimization of an off-Grid Hybrid Photovoltaic, Fuel Cell and Diesel Generator System. *Sustain Cities Soc* **2019**, *44*, 310–320, doi:10.1016/j.scs.2018.10.021.
- Calvin, K.; Dasgupta, D.; Krinner, G.; Mukherji, A.; Thorne, P.W.; Trisos, C.; Romero, J.; Aldunce, P.; Barrett, K.; Blanco, G.; et al. *IPCC*, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change; Geneva, Switzerland, 2023;
- 5. International Energy Agency (IEA) *Net Zero Roadmap A Global Pathway to Keep the* 1.5°C Goal in Reach; Paris, 2023;
- 6. Yolcan, O.O. World Energy Outlook and State of Renewable Energy: 10-Year Evaluation. *Innovation and Green Development* **2023**, *2*, 100070, doi:10.1016/j.igd.2023.100070.
- 7. International Energy Agency (IEA) *Electricity Market Report*; 2023;
- 8. Ramirez Camargo, L.; Valdes, J.; Masip Macia, Y.; Dorner, W. Assessment of On-Site Steady Electricity Generation from Hybrid Renewable Energy Systems in Chile. *Appl Energy* **2019**, *250*, 1548–1558, doi:10.1016/j.apenergy.2019.05.005.
- 9. Ministerio de Energía Plan de Descarbonización de La Matriz Eléctrica Available online: https://energia.gob.cl/mini-sitio/plan-de-descarbonizacion-de-la-matriz-electrica (accessed on 4 June 2021).
- Belaïd, F.; Al-Sarihi, A.; Al-Mestneer, R. Balancing Climate Mitigation and Energy Security Goals amid Converging Global Energy Crises: The Role of Green Investments. *Renew Energy* 2023, 205, 534–542, doi:10.1016/j.renene.2023.01.083.
- 11. Kostelac, M.; Pavić, I.; Capuder, T. Economic and Environmental Valuation of Green Hydrogen Decarbonisation Process for Price Responsive Multi-Energy Industry Prosumer. *Appl Energy* **2023**, *347*, 121484, doi:10.1016/j.apenergy.2023.121484.
- 12. Thomas, N. The Role of Hydrogen as a Future Fuel . **1988**, 72, 37–52.
- 13. Latarche, M. Oil Fuels Chemistry and Treatment. *Pounder's Marine Diesel Engines and Gas Turbines* **2021**, 117–149, doi:10.1016/B978-0-08-102748-6.00005-0.
- 14. Edwards, P.P.; Kuznetsov, V.L.; David, W.I.F.; Brandon, N.P. Hydrogen and Fuel Cells: Towards a Sustainable Energy Future. *Energy Policy* **2008**, *36*, 4356–4362, doi:10.1016/J.ENPOL.2008.09.036.
- 15. Hacker, V.; Mitsushima, S. Fuel Cells and Hydrogen: From Fundamentals to Applied Research; Elsevier, 2018; ISBN 9780128114599.
- 16. Johnson, R.T.; Biefeld, R.M.; Keck, J.D. Ionic Conductivity in Li5AlO4 and LiOH. *Mater Res Bull* **1977**, *12*, 577–587, doi:10.1016/0025-5408(77)90066-6.
- 17. Gobierno de Chile Estrategia Nacional Del Litio Por Chile y Su Gente; 2023;
- Cassir, M.; Meléndez-Ceballos, A.; Ringuedé, A.; Lair, V. 3. Molten Carbonate Fuel Cells . In *Compedium of Hydrogen Energy*; Woodhead Publishing: Sawston UK, 2016; Vol. 3, pp. 71–87.
- 19. Fan, L.; Tu, Z.; Chan, S.H. Recent Development of Hydrogen and Fuel Cell Technologies: A Review. *Energy Reports* **2021**, *7*, 8421–8446, doi:10.1016/j.egyr.2021.08.003.

- 20. Barckholtz, T.A.; Taylor, K.M.; Narayanan, S.; Jolly, S.; Ghezel-Ayagh, H. Molten Carbonate Fuel Cells for Simultaneous CO2 Capture, Power Generation, and H2 Generation. *Appl Energy* **2022**, *313*, 118553, doi:10.1016/j.apenergy.2022.118553.
- 21. Wee, J.-H. Contribution of Fuel Cell Systems to CO2 Emission Reduction in Their Application Fields. *Renewable and Sustainable Energy Reviews* **2010**, *14*, 735–744, doi:10.1016/j.rser.2009.10.013.
- 22. Wang, F.; Deng, S.; Zhang, H.; Wang, J.; Zhao, J.; Miao, H.; Yuan, J.; Yan, J. A Comprehensive Review on High-Temperature Fuel Cells with Carbon Capture. *Appl Energy* **2020**, *275*, 115342, doi:10.1016/J.APENERGY.2020.115342.
- 23. Mitsushima, S.; Gollas, B.; Hacker, V. Fuel Cells and Hydrogen; Elsevier, 2018;
- 24. Archer, S.A.; Steinberger-Wilckens, R. Systematic Analysis of Biomass Derived Fuels for Fuel Cells. *Int J Hydrogen Energy* **2018**, *43*, 23178–23192, doi:10.1016/J.IJHYDENE.2018.10.161.
- 25. Cigolotti, V.; Genovese, M.; Fragiacomo, P. Comprehensive Review on Fuel Cell Technology for Stationary Applications as Sustainable and Efficient Poly-Generation Energy Systems. *Energies (Basel)* **2021**, *14*, 4963, doi:10.3390/en14164963.
- 26. Da Rosa, A.V.; Ordóñez, J.C. Fuel Cells. In *Fundamentals of Renewable Energy Processes*; Academic Press, 2022; pp. 317–417 ISBN 978-0-12-816036-7.
- Haj Ibrahim, S.; Wejrzanowski, T.; Sobczak, P.; Cwieka, K.; Lysik, A.; Skibinski, J.; Oliver, G.J. Insight into Cathode Microstructure Effect on the Performance of Molten Carbonate Fuel Cell. *J Power Sources* 2021, 491, 229562, doi:10.1016/j.jpowsour.2021.229562.
- 28. Kim, S.H.; Miesse, C.M.; Lee, H.B.; Chang, I.W.; Hwang, Y.S.; Jang, J.H.; Cha, S.W. Ultra Compact Direct Hydrogen Fuel Cell Prototype Using a Metal Hydride Hydrogen Storage Tank for a Mobile Phone. *Appl Energy* **2014**, *134*, 382–391, doi:10.1016/j.apenergy.2014.08.019.
- 29. Piraino, F.; Fragiacomo, P. A Multi-Method Control Strategy for Numerically Testing a Fuel Cell-Battery-Supercapacitor Tramway. *Energy Convers Manag* **2020**, *225*, 113481, doi:10.1016/j.enconman.2020.113481.
- 30. Tomczyk, P. MCFC versus Other Fuel Cells—Characteristics, Technologies and Prospects. *J Power Sources* **2006**, *160*, 858–862, doi:10.1016/j.jpowsour.2006.04.071.
- Abdelkareem, M.A.; Lootah, M.A.; Sayed, E.T.; Wilberforce, T.; Alawadhi, H.; Yousef, B.A.A.; Olabi, A.G. Fuel Cells for Carbon Capture Applications. *Science of the Total Environment* 2021, 769, doi:10.1016/j.scitotenv.2020.144243.
- 32. Broers, G.H.J.; Schenke, M.; Piepers, G.G. High Temperature Galvanic Fuel Cells with Fused Carbonate Paste Electrolytes—I. General Considerations and Experimental Results. *Advanced Energy Conversion* **1964**, *4*, 131–147, doi:10.1016/0365-1789(64)90025-6.
- 33. Melendez-Ceballos, A. Adequacy of New Electrolyte Compositions and Nanostructured Protective Layers for the Cathode of Molten Carbonate Fuel Cells, Université Pierre et Marie Curie: Paris, 2017.
- 34. Samanta, S.; Ghosh, S. A Thermo-Economic Analysis of Repowering of a 250 MW Coal Fired Power Plant through Integration of Molten Carbonate Fuel Cell with Carbon Capture. *International Journal of Greenhouse Gas Control* **2016**, *51*, 48–55, doi:10.1016/J.IJGGC.2016.04.021.
- 35. Mastropasqua, L.; Spinelli, M.; Paganoni, A.; Campanari, S. Preliminary Design of a MW-Class Demo System for CO2 Capture with MCFC in a University Campus Cogeneration Plant. *Energy Procedia* **2017**, *126*, 453–460, doi:10.1016/J.EGYPRO.2017.08.213.

- 36. Makino, H.; Noda, N. Powder Technology and Nanotechnology Contributed for Clean Utilization of Coal. *Nanoparticle Technology Handbook* **2018**, 533–537, doi:10.1016/B978-0-444-64110-6.00031-7.
- Mehmeti, A.; Pedro Pérez-Trujillo, J.; Elizalde-Blancas, F.; Angelis-Dimakis, A.; McPhail, S.J. Exergetic, Environmental and Economic Sustainability Assessment of Stationary Molten Carbonate Fuel Cells. *Energy Convers Manag* 2018, *168*, 276–287, doi:10.1016/J.ENCONMAN.2018.04.095.
- 38. Abdollahipour, A.; Sayyaadi, H. Thermal Energy Recovery of Molten Carbonate Fuel Cells by Thermally Regenerative Electrochemical Cycles. *Energy* **2021**, *227*, 120489, doi:10.1016/J.ENERGY.2021.120489.
- More, A.; Pruthvi Deep, A.; Karmakar, S. Thermodynamic Analysis of a 500 MWe Coal-Fired Supercritical Thermal Power Plant Integrated with Molten Carbonate Fuel Cell (MCFC) at Flue Gas Stream. 2021, 645–654, doi:10.1007/978-981-15-5955-6\_60.
- 40. Uchida, I.; Hemmes, K.; Lindbergh, G.; Shores, D.; Selman, R. *Carbonate Fuel Cell Technology: Proceedings of the Fifth International Symposium*; The Electrochemical Society, Inc.: Pennington, New Jersey, 1999; Vol. 99–20; ISBN 1-56677-243-5.
- 41. Sartori da Silva, F.; Matelli, J.A. Exergoeconomic Analysis and Determination of Power Cost in MCFC Steam Turbine Combined Cycle. *Int J Hydrogen Energy* **2019**, *44*, 18293–18307, doi:10.1016/J.IJHYDENE.2019.05.156.
- 42. POSCO ENERGY Prepared Future H2; Seul;
- Lu, C.; Zhang, R.; Yang, G.; Huang, H.; Cheng, J.; Xu, S. Study and Performance Test of 10 KW Molten Carbonate Fuel Cell Power Generation System. *Int J Coal Sci Technol* 2021, 8, 368–376, doi:10.1007/s40789-021-00442-4.
- 44. Moreno, A.; McPhail, S.; Bravo, R. International Status of Molten Carbonate Fuel Cell (MCFC) Technology; Rome, 2008;
- 45. Lee, C.G.; Hwang, J.Y.; Oh, M.; Kim, D.H.; Lim, H.C. Overpotential Analysis with Various Anode Gas Compositions in a Molten Carbonate Fuel Cell. *J Power Sources* **2008**, *179*, 467–473, doi:10.1016/j.jpowsour.2007.12.125.
- 46. Kulkarni, A.; Giddey, S. Materials Issues and Recent Developments in Molten Carbonate Fuel Cells. *Journal of Solid State Electrochemistry 2012 16:10* **2012**, *16*, 3123–3146, doi:10.1007/S10008-012-1771-Y.
- 47. Czelej, K.; Cwieka, K.; Colmenares, J.C.; Kurzydlowski, K.J. Catalytic Activity of NiO Cathode in Molten Carbonate Fuel Cells. *Appl Catal B* **2018**, *222*, 73–75, doi:10.1016/J.APCATB.2017.10.003.
- 48. Czelej, K.; Cwieka, K.; Colmenares, J.C.; Kurzydlowski, K.J. Atomistic Insight into the Electrode Reaction Mechanism of the Cathode in Molten Carbonate Fuel Cells. *J Mater Chem A Mater* **2017**, *5*, 13763–13768, doi:10.1039/C7TA02011B.
- Czelej, K.; Cwieka, K.; Wejrzanowski, T.; Spiewak, P.; Kurzydlowski, K.J. Decomposition of Activated CO2 Species on Ni(110): Role of Surface Diffusion in the Reaction Mechanism. *Catal Commun* 2016, 74, 65–70, doi:10.1016/J.CATCOM.2015.10.034.
- 50. Corradini, D.; Coudert, F.X.; Vuilleumier, R. Carbon Dioxide Transport in Molten Calcium Carbonate Occurs through an Oxo-Grotthuss Mechanism via a Pyrocarbonate Anion. *Nature Chemistry 2016 8:5* **2016**, *8*, 454–460, doi:10.1038/nchem.2450.
- 51. Ghassemi, M.; Kamvar, Majid.; Steinberger-Wilckens, Robert. *Fundamentals of Heat and Fluid Flow in High Temperature Fuel Cells*; Academic Press, 2020; ISBN 9780128157534.

- 52. Lei, X.; Haines, K.; Huang, K.; Qin, C. Density Functional Theory Study of Oxygen Migration in Molten Carbonate. *J Power Sources* **2016**, *305*, 161–166, doi:10.1016/J.JPOWSOUR.2015.11.095.
- 53. Bergaglio, E.; Sabattini, A.; Capobianco, P. Research and Development on Porous Components for MCFC Applications. *J Power Sources* **2005**, *149*, 63–65, doi:10.1016/j.jpowsour.2005.01.033.
- 54. Sheikh, A.A.; Bianchi, F.R.; Bove, D.; Bosio, B. A Review on MCFC Matrix: State-ofthe-Art, Degradation Mechanisms and Technological Improvements. *Heliyon* **2024**, *10*, e25847, doi:10.1016/j.heliyon.2024.e25847.
- 55. Lair, V.; Albin, V.; Ringuedé, A.; Cassir, M. Theoretical Predictions vs. Experimental Measurements of the Electrical Conductivity of Molten Li2CO3-K2CO3 Modified by Additives. In Proceedings of the International Journal of Hydrogen Energy; Pergamon, December 1 2012; Vol. 37, pp. 19357–19364.
- 56. Meléndez-Ceballos, A.; Albin, V.; Crapart, C.; Lair, V.; Ringuedé, A.; Cassir, M. Influence of Cs and Rb Additions in Li–K and Li–Na Molten Carbonates on the Behaviour of MCFC Commercial Porous Ni Cathode. *Int J Hydrogen Energy* **2017**, *42*, 1853–1858, doi:10.1016/j.ijhydene.2016.09.118.
- 57. Ricca, C.; Ringuedé, A.; Cassir, M.; Adamo, C.; Labat, F. Mixed Lithium-Sodium (LiNaCO3) and Lithium-Potassium (LiKCO3) Carbonates for Low Temperature Electrochemical Applications: Structure, Electronic Properties and Surface Reconstruction from Ab-Initio Calculations. *Surf Sci* **2016**, *647*, 66–77, doi:10.1016/J.SUSC.2015.12.027.
- Accardo, G.; Frattini, D.; Yoon, S.P.; Ham, H.C.; Nam, S.W. Performance and Properties of Anodes Reinforced with Metal Oxide Nanoparticles for Molten Carbonate Fuel Cells. *J Power Sources* 2017, 370, 52–60, doi:10.1016/j.jpowsour.2017.10.015.
- Accardo, G.; Frattini, D.; Moreno, A.; Yoon, S.P.; Han, J.H.; Nam, S.W. Influence of Nano Zirconia on NiAl Anodes for Molten Carbonate Fuel Cell: Characterization, Cell Tests and Post-Analysis. *J Power Sources* 2017, 338, 74–81, doi:10.1016/j.jpowsour.2016.11.029.
- 60. Frattini, D.; Accardo, G.; Moreno, A.; Yoon, S.P.; Han, J.H.; Nam, S.W. A Novel Nickel-Aluminum Alloy with Titanium for Improved Anode Performance and Properties in Molten Carbonate Fuel Cells. *J Power Sources* **2017**, *352*, 90–98, doi:10.1016/j.jpowsour.2017.03.112.
- 61. Youn, J.Y.; Yoon, S.P.; Han, J.; Nam, S.W.; Lim, T.H.; Hong, S.A.; Lee, K.Y. Fabrication and Characteristics of Anode as an Electrolyte Reservoir for Molten Carbonate Fuel Cell. *J Power Sources* **2006**, *157*, 121–127, doi:10.1016/j.jpowsour.2005.07.068.
- Wejrzanowski, T.; Cwieka, K.; Skibinski, J.; Lysik, A.; Ibrahim, S.H.; Milewski, J.; Xing, W.; Lee, C.G. Microstructure Driven Design of Porous Electrodes for Molten Carbonate Fuel Cell Application: Recent Progress. *Int J Hydrogen Energy* 2020, *45*, 25719–25732, doi:10.1016/J.IJHYDENE.2019.12.038.
- 63. Lee, C.-G.; Hwang, J.-Y.; Lee, S.-Y.; Oh, M.; Kim, D.-H.; Lim, H.-C. Effect of Anode Area on the Cell Performance in a Molten Carbonate Fuel Cell. *J Electrochem Soc* 2008, *155*, A138, doi:10.1149/1.2815573/PDF.
- 64. Bie, K.; Fu, P.; Liu, Y.; Muhammad, A. Comparative Study on the Performance of Different Carbon Fuels in a Molten Carbonate Direct Carbon Fuel Cell with a Novel Anode Structure. *J Power Sources* **2020**, *460*, 228101, doi:10.1016/J.JPOWSOUR.2020.228101.

- 65. Kawase, M. Manufacturing Method for Tubular Molten Carbonate Fuel Cells and Basic Cell Performance. *J Power Sources* **2015**, 285, 260–265, doi:10.1016/j.jpowsour.2015.03.117.
- 66. Wee, J.-H.; Song, D.-J.; Jun, C.-S.; Lim, T.-H.; Hong, S.-A.; Lim, H.-C.; Lee, K.-Y. Evaluation of Ni–Ni3Al(5wt.%)–Al(3wt.%) as an Anode Electrode for Molten Carbonate Fuel Cell. *J Alloys Compd* **2005**, *390*, 155–160, doi:10.1016/j.jallcom.2004.06.103.
- Nguyen, H.V.P.; Song, S.A.; Seo, D.; Park, D.N.; Ham, H.C.; Oh, I.H.; Yoon, S.P.; Han, J.; Nam, S.W.; Kim, J. Fabrication of Ni-Al-Cr Alloy Anode for Molten Carbonate Fuel Cells. *Mater Chem Phys* 2012, *136*, 910–916, doi:10.1016/j.matchemphys.2012.08.018.
- 68. Li, C.; Chen, J.; Li, W.; Hu, Y.; Ren, Y.; Qiu, W.; He, J.; Chen, J. Investigation on Compressive Behavior of Cu-35Ni-15Al Alloy at High Temperatures. *Materials Science-Poland* **2014**, *32*, 341–349, doi:10.2478/s13536-014-0203-3.
- 69. Özkan, G.; İyidir, U.C. Synthesis and Characterization of Molten Carbonate Fuel Cell Anode Materials. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **2015**, *37*, 2487–2495, doi:10.1080/15567036.2011.627415.
- 70. Lee, E.-K.; Chun, H.H.; Kim, Y.-T. Enhancing Ni Anode Performance via Gd2O3 Addition in Molten Carbonate-Type Direct Carbon Fuel Cell. *Int J Hydrogen Energy* **2014**, *39*, 16541–16547, doi:10.1016/j.ijhydene.2014.03.180.
- 71. Meléndez-Ceballos, A.; Fernández-Valverde, S.M.; Albin, V.; Lair, V.; Chávez-Carvayar, J.Á.; Ringuedé, A.; Cassir, M. Investigation on Niobium Oxide Coatings for Protecting and Enhancing the Performance of Ni Cathode in the MCFC. *Int J Hydrogen Energy* 2016, 41, 18721–18731, doi:10.1016/j.ijhydene.2016.04.045.
- 72. Li, W.; Chen, J.; Liang, H.; Li, C. Research on High-Temperature Compression and Creep Behavior of Porous Cu–Ni–Cr Alloy for Molten Carbonate Fuel Cell Anodes. *Materials Science-Poland* **2015**, *33*, 356–362, doi:10.1515/msp-2015-0059.
- 73. Nosewicz, S.; Jurczak, G.; Wejrzanowski, T.; Ibrahim, S.H.; Grabias, A.; Węglewski, W.; Kaszyca, K.; Rojek, J.; Chmielewski, M. Thermal Conductivity Analysis of Porous NiAl Materials Manufactured by Spark Plasma Sintering: Experimental Studies and Modelling. *Int J Heat Mass Transf* **2022**, *194*, 123070, doi:10.1016/j.ijheatmasstransfer.2022.123070.
- 74. Devianto, H.; Li, Z.; Yoon, S.P.; Han, J.; Nam, S.W.; Lim, T.-H.; Lee, H.-I. The Effect of Electrolyte Wettability on Reforming Catalyst in Direct Ethanol MCFC. *Current Applied Physics* **2010**, *10*, S26–S28, doi:10.1016/j.cap.2009.11.009.
- Kim, Y.-S.; Lee, K.-Y.; Chun, H.-S. Creep Characteristics of Porous Ni/Ni3Al Anodes for Molten Carbonate Fuel Cells. *J Power Sources* 2001, 99, 26–33, doi:10.1016/S0378-7753(00)00689-3.
- Hwang, E.R.; Park, J.W.; Kim, Y.D.; Kim, S.J.; Kang, S.G. Effect of Alloying Elements on the Copper-Base Anode for Molten Carbonate Fuel Cells. *J Power Sources* 1997, 69, 55–60, doi:10.1016/S0378-7753(97)02566-4.
- 77. Li, G.; Thomas, B.G.; Stubbins, J.F. Modeling Creep and Fatigue of Copper Alloys. *Metall Mater Trans A Phys Metall Mater Sci* **2000**, *31*, 2491–2502, doi:10.1007/s11661-000-0194-z.
- 78. Klassert, A.; Tikana, L. Copper and Copper–Nickel Alloys an Overview. *Corrosion Behaviour and Protection of Copper and Aluminium Alloys in Seawater* **2007**, 47–61, doi:10.1533/9781845693084.2.47.
- 79. Martínez, C.; Briones, F.; Rojas, P.; Ordoñez, S.; Aguilar, C.; Guzmán, D. Microstructure and Mechanical Properties of Copper, Nickel and Ternary Alloys Cu-Ni-Zr Obtained by Mechanical Alloying and Hot Pressing. *MRS Adv* **2017**, *2*, 2831–2836, doi:10.1557/ADV.2017.519.

- 80. Hume-Rothery, W. The Structure of Metals and Alloys. *Nature* **1936**, *138*, 7–8, doi:10.1038/138007a0.
- 81. Pero-Sanz Elorz, J.A.; Quintana Hernández, M.J.; Verdeja González, L.F. Total Insolubility and Solubility in Alloys. In *Solidification and Solid-State Transformations of Metals and Alloys*; Elsevier, 2017; pp. 67–92.
- 82. Ren, Y.; Peng, Y.; Chen, J.; Qiu, W.; Li, W.; Li, C.; Niu, Y. Electrochemical Impedance Studies on the Corrosion of Cu-35Ni-10Al Alloy in a Molten (0.62Li, 0.38K) 2 CO 3 Environment. *Int. J. Electrochem. Sci* **2019**, *14*, 6147–6153, doi:10.20964/2019.07.49.
- 83. Parameswaran, P.; Godwin Antony, A.; Dinesh, S.; Radhakrishnan, K. Experimental Study on Mechanical and Corrosion Characteristics of Nab Alloy with the Addition of Chromium. *Mater Today Proc* **2018**, *5*, 8089–8094, doi:10.1016/j.matpr.2017.11.495.
- 84. de Miguel, M.T.; Lasanta, M.I.; García-Martín, G.; Díaz, R.; Pérez, F.J. Temperature Effect and Alloying Elements Impact on the Corrosion Behaviour of the Alloys Exposed to Molten Carbonate Environments for CSP Application. *Corros Sci* **2022**, *201*, 110274, doi:10.1016/j.corsci.2022.110274.
- Liu, M.; Wang, S.; Chen, T.; Yuan, C.; Zhou, Y.; Wang, S.; Huang, J. Performance of the Nano-Structured Cu-Ni (Alloy) -CeO2 Anode for Solid Oxide Fuel Cells. *J Power Sources* 2015, 274, 730–735, doi:10.1016/j.jpowsour.2014.10.122.
- 86. Meléndez-Ceballos, A.; Albin, V.; Fernández-Valverde, S.M.; Ringuedé, A.; Cassir, M. Electrochemical Properties of Atomic Layer Deposition Processed CeO 2 as a Protective Layer for the Molten Carbonate Fuel Cell Cathode. *Electrochim Acta* **2014**, *140*, 174–181, doi:10.1016/j.electacta.2014.05.025.
- 87. Rieder, H.; Dillhöfer, A.; Spies, M.; Bamberg, J.; Hess, T. Online Monitoring of Additive Manufacturing Processes Using Ultrasound. **2016**.
- Yushin, D.I.; Smirnov, A.V.; Solis Pinargote, N.W.; Peretyagin, P.Y.; Torrecillas San Millan, R. Modeling Process of Spark Plasma Sintering of Powder Materials by Finite Element Method. *Materials Science Forum* 2015, 834, 41–50, doi:10.4028/www.scientific.net/MSF.834.41.
- 89. Qin, Z.; Zhang, Q.; Luo, Q.; Wu, Z.; Shen, B.; Liu, L.; Hu, W. Microstructure Design to Improve the Corrosion and Cavitation Corrosion Resistance of a Nickel-Aluminum Bronze. *Corros Sci* **2018**, *139*, 255–266, doi:10.1016/j.corsci.2018.04.043.
- 90. Richardson, I. Guide to Nickel Aluminium Bronze for Engineers. *Copper Development* Association **2016**, 100.
- Arcos, C.; Ramos-Grez, J.A.; Sancy, M.; La Fé-Perdomo, I.; Setchi, R.; Guerra, C. Suitability of Nickel Aluminium Bronze Alloy Fabricated by Laser Powder Bed Fusion to Be Used in the Marine Environment. *Corros Sci* 2024, 226, 111656, doi:10.1016/j.corsci.2023.111656.
- 92. ASTM ASTM G1-03 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens; 2017;
- 93. Meléndez-Ceballos, A.; Albin, V.; Lair, V.; Ringuedé, A.; Cassir, M. A Kinetic Approach on the Effect of Cs Addition on Oxygen Reduction for MCFC Application. *Electrochim Acta* **2015**, *184*, 295–300, doi:10.1016/j.electacta.2015.10.057.
- 94. Moutiers, G.; Cassir, M.; Piolet, C.; Devynck, J. Thermodynamic and Voltammetric Study of Oxygen Systems in Molten Na2CO3K2CO3 (56-44 Mol.%) Eutectic at 750°C. *Electrochim Acta* **1991**, *36*, 1063–1071, doi:10.1016/0013-4686(91)85316-Y.
- 95. Acar, C.; Dincer, I. The Potential Role of Hydrogen as a Sustainable Transportation Fuel to Combat Global Warming. *Int J Hydrogen Energy* **2020**, *45*, 3396–3406, doi:10.1016/j.ijhydene.2018.10.149.

- 96. Wee, J.H. Carbon Dioxide Emission Reduction Using Molten Carbonate Fuel Cell Systems. *Renewable and Sustainable Energy Reviews* **2014**, *32*, 178–191, doi:10.1016/J.RSER.2014.01.034.
- 97. Ceccanti, F.; Giorgetti, A.; Citti, P. A Support Structure Design Strategy for Laser Powder Bed Fused Parts. *Procedia Structural Integrity* **2019**, *24*, 667–679, doi:10.1016/j.prostr.2020.02.059.
- 98. Gera, D.; Santos, J.; Kiminami, C.S.; Gaargarella, P. Comparison of Cu–Al–Ni–Mn–Zr Shape Memory Alloy Prepared by Selective Laser Melting and Conventional Powder Metallurgy. *Transactions of Nonferrous Metals Society of China* **2020**, *30*, 3322–3332, doi:10.1016/S1003-6326(20)65464-4.
- 99. ASTM C373 88 Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products; 2006;
- 100. Scanning Electron Microscope (Quanta 250 FEG) Available online: https://www.bose.res.in/facilities/Technical\_Cell/sem.html (accessed on 8 November 2021).
- 101. Hooper, P.A. Melt Pool Temperature and Cooling Rates in Laser Powder Bed Fusion. *Addit Manuf* 2018, 22, 548–559, doi:10.1016/j.addma.2018.05.032.
- 102. Zhang, M.-X.; Kelly, P.M. Crystallography of Spheroidite and Tempered Martensite. *Acta Mater* **1998**, *46*, 4081–4091, doi:10.1016/S1359-6454(98)00046-9.
- 103. Liu, Y.; Ye, Z.; Wang, X.; Liang, B.; Zhang, Y. Microstructure and Mechanical Behavior of Cu–9Al–4Ni-3.5Fe-0.5Mn Alloy Fabricated by Laser Melting Deposition. *Materials Science and Engineering: A* 2021, 826, 142006, doi:10.1016/j.msea.2021.142006.
- 104. Orzolek, S.M.; Semple, J.K.; Fisher, C.R. Influence of Processing on the Microstructure of Nickel Aluminum Bronze (NAB). *Addit Manuf* **2022**, *56*, 102859, doi:10.1016/j.addma.2022.102859.
- 105. Culpan, E.A.; Rose, G. Microstructural Characterization of Cast Nickel Aluminium Bronze. *J Mater Sci* **1978**, *13*, 1647–1657, doi:10.1007/BF00548728.
- 106. Brezina, P. Heat Treatment of Complex Aluminium Bronzes. *International Metals Reviews* **1982**, 27, 77–120, doi:10.1179/imr.1982.27.1.77.
- 107. Tavares, S.S.M.; Mota, N.M.; da Igreja, H.R.; Barbosa, C.; Pardal, J.M. Microstructure, Mechanical Properties, and Brittle Fracture of a Cast Nickel-Aluminum-Bronze (NAB) UNS C95800. *Eng Fail Anal* 2021, *128*, 105606, doi:10.1016/j.engfailanal.2021.105606.
- 108. Dareh Baghi, A.; Nafisi, S.; Hashemi, R.; Ebendorff-Heidepriem, H.; Ghomashchi, R. Effective Post Processing of SLM Fabricated Ti-6A1-4 V Alloy: Machining vs Thermal Treatment. *J Manuf Process* 2021, 68, 1031–1046, doi:10.1016/j.jmapro.2021.06.035.
- 109. Gupta, S.K.; Mao, Y. A Review on Molten Salt Synthesis of Metal Oxide Nanomaterials: Status, Opportunity, and Challenge. *Prog Mater Sci* **2021**, *117*, 100734, doi:10.1016/j.pmatsci.2020.100734.
- 110. Audigié, P.; Encinas-Sánchez, V.; Juez-Lorenzo, M.; Rodríguez, S.; Gutiérrez, M.; Pérez, F.J.; Agüero, A. High Temperature Molten Salt Corrosion Behavior of Aluminide and Nickel-Aluminide Coatings for Heat Storage in Concentrated Solar Power Plants. *Surf Coat Technol* 2018, 349, 1148–1157, doi:10.1016/j.surfcoat.2018.05.081.
- 111. Vossen, J.P.T.; Janssen, A.H.H.; de Wit, J.H.W. Corrosion Behavior of Nickel-Iron Alloys in Molten Carbonate. *J Electrochem Soc* **1996**, *143*, 58–66, doi:10.1149/1.1836387.
- 112. Tang, D.; Zheng, K.; Yin, H.; Mao, X.; Sadoway, D.R.; Wang, D. Electrochemical Growth of a Corrosion-Resistant Multi-Layer Scale to Enable an Oxygen-Evolution Inert Anode in Molten Carbonate. *Electrochim Acta* 2018, 279, 250–257, doi:10.1016/j.electacta.2018.05.095.

- 113. Zheng, K.; Du, K.; Cheng, X.; Jiang, R.; Deng, B.; Zhu, H.; Wang, D. Nickel-Iron-Copper Alloy as Inert Anode for Ternary Molten Carbonate Electrolysis at 650°C. *J Electrochem Soc* 2018, *165*, E572–E577, doi:10.1149/2.1211811jes.
- 114. Hasegawa, M. Ellingham Diagram. *Treatise on Process Metallurgy* **2014**, *1*, 507–516, doi:10.1016/B978-0-08-096986-2.00032-1.
- Spiegel, M.; Biedenkopf, P.; Grabke, H.J. Corrosion of Iron Base Alloys and High Alloy Steels in the Li2CO3-K2CO3 Eutectic Mixture. *Corros Sci* 1997, *39*, 1193–1210, doi:10.1016/S0010-938X(97)00020-6.
- 116. Luo, J.; Deng, C.K.; Tariq, N. ul H.; Li, N.; Han, R.F.; Liu, H.H.; Wang, J.Q.; Cui, X.Y.; Xiong, T.Y. Corrosion Behavior of SS316L in Ternary Li2CO3–Na2CO3–K2CO3 Eutectic Mixture Salt for Concentrated Solar Power Plants. *Solar Energy Materials and Solar Cells* 2020, 217, 110679, doi:10.1016/j.solmat.2020.110679.
- 117. Goupil, G.; Bonnefont, G.; Idrissi, H.; Guay, D.; Roué, L. Consolidation of Mechanically Alloyed Cu–Ni–Fe Material by Spark Plasma Sintering and Evaluation as Inert Anode for Aluminum Electrolysis. J Alloys Compd 2013, 580, 256–261, doi:10.1016/j.jallcom.2013.05.128.
- Alkelae, F.; Sasaki, S. Microstructures Generated by Nickel Aluminium Bronze Alloy L-PBFed and Their Effect on Tribological and Mechanical Properties. *Jurnal Tribologi* 2021, 29, 41–56.
- Lv, Y.; Ding, Y.; Han, Y.; Zhang, L.-C.; Wang, L.; Lu, W. Strengthening Mechanism of Friction Stir Processed and Post Heat Treated NiAl Bronze Alloy: Effect of Rotation Rates. *Materials Science and Engineering: A* 2017, 685, 439–446, doi:10.1016/j.msea.2016.12.050.
- 120. Ashby, M.F.; Evans, A.; Fleck, N.A.; Gibson, L.J.; Hutchinson, J.W.; Wadley, H.N.G. Metal Foams: A Design Guide. *Mater Des* 2002, 23, 119, doi:10.1016/S0261-3069(01)00049-8.
- 121. Förster, W.; Pucklitzsch, T.; Dietrich, D.; Nickel, D. Mechanical Performance of Hexagonal Close-Packed Hollow Sphere Infill Structures with Shared Walls under Compression Load. *Addit Manuf* **2022**, *59*, 103135, doi:10.1016/j.addma.2022.103135.
- 122. Choe, H.; Dunand, D.C. Creep of Ni-Al and Ni-Cr-Al Superalloy Foams. In Affordable Metal Matrix Composites for High Performance Applications II; 2003.
- 123. Gomez-Vidal, J.C.; Noel, J.; Weber, J. Corrosion Evaluation of Alloys and MCrAlX Coatings in Molten Carbonates for Thermal Solar Applications. *Solar Energy Materials and Solar Cells* **2016**, *157*, 517–525, doi:10.1016/j.solmat.2016.07.029.
- 124. Öztürk, S.; Sünbül, S.E.; Metoğlu, A.; Önal, S.; İçin, K. Characterisation of Nickel– Aluminium Bronze Powders Produced by the Planar Flow Casting Method. *Materials Science and Technology* **2020**, *36*, 1771–1784, doi:10.1080/02670836.2020.1834681.
- 125. Karfidov, E.; Nikitina, E.; Erzhenkov, M.; Seliverstov, K.; Chernenky, P.; Mullabaev, A.; Tsvetov, V.; Mushnikov, P.; Karimov, K.; Molchanova, N.; et al. Corrosion Behavior of Candidate Functional Materials for Molten Salts Reactors in LiF–NaF–KF Containing Actinide Fluoride Imitators. *Materials* **2022**, *15*, 761, doi:10.3390/ma15030761.
- 126. Adeloju, s. B.; Duan, Y.Y. Corrosion Resistance of Cu2 O and CuO on Copper Surfaces in Aqueous Media. *British Corrosion Journal* **1994**, *29*, 309–314, doi:10.1179/000705994798267485.
- 127. Nanadegani, F.S.; Sunden, B. Review of Exergy and Energy Analysis of Fuel Cells. *Int J Hydrogen Energy* **2023**, doi:10.1016/j.ijhydene.2023.05.052.
- 128. Sharaf, O.Z.; Orhan, M.F. An Overview of Fuel Cell Technology: Fundamentals and Applications. *Renewable and Sustainable Energy Reviews* **2014**, *32*, 810–853, doi:10.1016/j.rser.2014.01.012.

- 129. Ming, W.; Sun, P.; Zhang, Z.; Qiu, W.; Du, J.; Li, X.; Zhang, Y.; Zhang, G.; Liu, K.; Wang, Y.; et al. A Systematic Review of Machine Learning Methods Applied to Fuel Cells in Performance Evaluation, Durability Prediction, and Application Monitoring. *Int J Hydrogen Energy* 2023, 48, 5197–5228, doi:10.1016/j.ijhydene.2022.10.261.
- 130. Olabi, A.G.; Wilberforce, T.; Sayed, E.T.; Elsaid, K.; Abdelkareem, M.A. Prospects of Fuel Cell Combined Heat and Power Systems. *Energies (Basel)* **2020**, *13*, 1–20, doi:10.3390/en13164104.
- 131. Shuhayeu, P.; Martsinchyk, A.; Martsinchyk, K.; Szczęśniak, A.; Szabłowski, Ł.; Dybiński, O.; Milewski, J. Model-Based Quantitative Characterization of Anode Microstructure and Its Effect on the Performance of Molten Carbonate Fuel Cell. *Int J Hydrogen Energy* 2023, doi:10.1016/j.ijhydene.2023.05.175.
- 132. Arcos, C.; Guerra, C.; Ramos-Grez, J.A.; Sancy, M. Ni-Al Bronze in Molten Carbonate Manufactured by LPBF: Effect of Porosity Design on Mechanical Properties and Oxidation. *Materials* **2023**, *16*, doi:10.3390/ma16103893.
- 133. Saber, D.; El-Aziz, K.A.; Felemban, B.F.; Alghtani, A.H.; Ali, H.T.; Ahmed, E.M.; Megahed, M. Characterization and Performance Evaluation of Cu-Based/TiO2 Nano Composites. *Sci Rep* **2022**, *12*, 1–14, doi:10.1038/s41598-022-10616-y.
- 134. Frattini, D.; Accardo, G.; Moreno, A.; Yoon, S.P.; Han, J.H.; Nam, S.W. Strengthening Mechanism and Electrochemical Characterization of ZrO2 Nanoparticles in Nickel– Aluminum Alloy for Molten Carbonate Fuel Cells. *Journal of Industrial and Engineering Chemistry* **2017**, *56*, 285–291, doi:10.1016/j.jiec.2017.07.021.
- 135. Gonzalez-Rodriguez, J.G.; Mejia, E.; Rosales, I.; Salinas-Bravo, V.M.; Rosas, G.; MArtinez-Villafañe, A. Effect of Heat Treatment and Chemical Composition on the Corrosion Behavior of Ni-Al Intermetallics in Molten (Li + K) Carbonate. J Power Sources 2008, 176, 215–221, doi:10.1016/j.jpowsour.2007.10.045.
- 136. Briones, F.; Seriacopi, V.; Martínez, C.; Valin, J.L.; Centeno, D.; Machado, I.F. The Effects of Pressure and Pressure Routes on the Microstructural Evolution and Mechanical Properties of Sintered Copper via SPS. *Journal of Materials Research and Technology* 2023, 25, 2455–2470, doi:10.1016/j.jmrt.2023.06.099.
- 137. Zawrah, M.F.; Zayed, H.A.; Essawy, R.A.; Nassar, A.H.; Taha, M.A. Preparation by Mechanical Alloying, Characterization and Sintering of Cu-20wt.% Al2O3 Nanocomposites. *Mater Des* **2013**, *46*, 485–490, doi:10.1016/j.matdes.2012.10.032.
- 138. Zhang, Z.; Chen, D.L. Contribution of Orowan Strengthening Effect in Particulate-Reinforced Metal Matrix Nanocomposites. *Materials Science and Engineering: A* 2008, 483–484, 148–152, doi:10.1016/j.msea.2006.10.184.
- 139. Meléndez-Ceballos, A.; Albin, V.; Fernández-Valverde, S.M.; Ringuedé, A.; Cassir, M. Electrochemical Properties of Atomic Layer Deposition Processed CeO2 as a Protective Layer for the Molten Carbonate Fuel Cell Cathode. *Electrochim Acta* **2014**, *140*, 174–181, doi:10.1016/j.electacta.2014.05.025.
- Pineda, F.; Walczak, M.; Vilchez, F.; Guerra, C.; Escobar, R.; Sancy, M. Evolution of Corrosion Products on ASTM A36 and AISI 304L Steels Formed in Exposure to Molten NaNO3–KNO3 Eutectic Salt: Electrochemical Study. *Corros Sci* 2022, *196*, 110047, doi:10.1016/j.corsci.2021.110047.
- 141. Martínez, C.; Guerra, C.; Silva, D.; Cubillos, M.; Briones, F.; Muñoz, L.; Páez, M.A.; Aguilar, C.; Sancy, M. Effect of Porosity on Mechanical and Electrochemical Properties of Ti–6Al–4V Alloy. *Electrochim Acta* 2020, 338, 135858, doi:10.1016/j.electacta.2020.135858.

- 142. Valverde, B.; Sancy, M.; Martínez, C.; Botello, E.; Pío, E.; Aguilar, C. Effect of Sn Content on the Passivity of Ti-Ta-Sn Alloys. *Corros Sci* **2023**, *211*, 110887, doi:10.1016/j.corsci.2022.110887.
- 143. Orazem, M.E.; Tribollet, B. Constant-Phase Elements. In *Electrochemical Impedance Spectroscopy*; 2017; pp. 395–419 ISBN 9781118527399.
- 144. Tribollet, B.; Vivier, V.; Orazem, M.E. *EIS Technique in Passivity Studies: Determination of the Dielectric Properties of Passive Films*; Wandelt, K., Ed.; Elsevier.; 2018; ISBN 9780128098943.
- 145. Hirschorn, B.; Orazem, M.E.; Tribollet, B.; Vivier, V.; Frateur, I.; Musiani, M. Constant-Phase-Element Behavior Caused by Resistivity Distributions in Films: II. Applications. J Electrochem Soc 2010, 157, C458, doi:10.1149/1.3499565.
- 146. Wang, P.; Du, K.; Yin, H.; Wang, D. Corrosion and Protection of Metallic Materials in Molten Carbonates for Concentrating Solar Power and Molten Carbonate Electrolysis Applications. *Corrosion Communications* 2023, 11, 58–71, doi:10.1016/j.corcom.2023.01.003.
- 147. Grosu, Y.; Anagnostopoulos, A.; Navarro, M.E.; Ding, Y.; Faik, A. Inhibiting Hot Corrosion of Molten Li2CO3-Na2CO3-K2CO3 Salt through Graphitization of Construction Materials for Concentrated Solar Power. *Solar Energy Materials and Solar Cells* 2020, 215, 110650, doi:10.1016/j.solmat.2020.110650.
- 148. Grosu, Y.; Anagnostopoulos, A.; Balakin, B.; Krupanek, J.; Navarro, M.E.; González-Fernández, L.; Ding, Y.; Faik, A. Nanofluids Based on Molten Carbonate Salts for High-Temperature Thermal Energy Storage: Thermophysical Properties, Stability, Compatibility and Life Cycle Analysis. *Solar Energy Materials and Solar Cells* 2021, 220, 110838, doi:10.1016/j.solmat.2020.110838.
- 149. González-Fernández, L.; Intxaurtieta-Carcedo, M.; Bondarchuk, O.; Grosu, Y. Effect of Dynamic Conditions on High-Temperature Corrosion of Ternary Carbonate Salt for Thermal Energy Storage Applications. *Solar Energy Materials and Solar Cells* 2022, 240, 111666, doi:10.1016/j.solmat.2022.111666.
- 150. González-Fernández, L.; Anagnostopoulos, A.; Karkantonis, T.; Bondarchuk, O.; Dimov, S.; Chorążewski, M.; Ding, Y.; Grosu, Y. Laser-Induced Carbonization of Stainless Steel as a Corrosion Mitigation Strategy for High-Temperature Molten Salts Applications. J Energy Storage 2022, 56, 105972, doi:10.1016/j.est.2022.105972.
- 151. González-Fernández, L.; Anagnostopoulos, A.; Karkantonis, T.; Dimov, S.; Chorążewski, M.; Ding, Y.; Grosu, Y. Laser-Texturing of Stainless Steel as a Corrosion Mitigation Strategy for High-Temperature Molten Salts Applications under Dynamic Conditions. *Solar Energy Materials and Solar Cells* **2023**, 257, 112380, doi:10.1016/j.solmat.2023.112380.
- 152. Fernández, A.G.; Cabeza, L.F. Corrosion Monitoring and Mitigation Techniques on Advanced Thermal Energy Storage Materials for CSP Plants. *Solar Energy Materials and Solar Cells* **2019**, *192*, 179–187, doi:10.1016/j.solmat.2018.12.028.
- 153. Fernández, A.G.; Pineda, F.; Walczak, M.; Cabeza, L.F. Corrosion Evaluation of Alumina-Forming Alloys in Carbonate Molten Salt for CSP Plants. *Renew Energy* **2019**, *140*, 227–233, doi:10.1016/j.renene.2019.03.087.
- 154. Chen, X.; Zhao, Z.; Qu, J.; Zhang, B.; Ding, X.; Geng, Y.; Xie, H.; Wang, D.; Yin, H. Electrolysis of Lithium-Free Molten Carbonates. *ACS Sustain Chem Eng* **2021**, *9*, 4167–4174, doi:10.1021/acssuschemeng.1c00028.
- 155. Yang, Z.; Du, K.; Wang, P.; Yin, H.; Wang, D. Effect of Borate on the Corrosion Behaviors of Ni11Fe10Cu Anode in Molten Carbonate. *Corros Sci* **2023**, *223*, 111459, doi:10.1016/j.corsci.2023.111459.

- Chen, H.; Li, B.; Wen, B.; Ye, Q.; Zhang, N. Corrosion Resistance of Iron-Chromium-Aluminium Steel in Eutectic Molten Salts under Thermal Cycling Conditions. *Corros Sci* 2020, 173, 108798, doi:10.1016/j.corsci.2020.108798.
- 157. Perissi, I.; Bardi, U.; Caporali, S.; Lavacchi, A. High Temperature Corrosion Properties of Ionic Liquids. *Corros Sci* **2006**, *48*, 2349–2362, doi:10.1016/j.corsci.2006.06.010.
- Feng, X.K.; Melendres, C.A. Anodic Corrosion and Passivation Behavior of Some Metals in Molten LiCl - KCl Containing Oxide Ions. *J Electrochem Soc* 1982, 129, 1245–1249, doi:10.1149/1.2124095.
- 159. Benito, N.; Flores, M. Evidence of Mixed Oxide Formation on the Cu/SiO2 Interface. *The Journal of Physical Chemistry C* **2017**, *121*, 18771–18778, doi:10.1021/acs.jpcc.7b06563.
- Özel, T.; Arisoy, Y.M. Experimental and Numerical Investigations on Machining Induced Surface Integrity in Inconel-100 Nickel-Base Alloy. *Procedia CIRP* 2014, 13, 302–307, doi:10.1016/j.procir.2014.04.051.
- 161. Ponomarova, S.; Odnosum, V.; Koval, I.; Monastyrsky, G.; Kolomytsev, V.; Ochin, P.; Portier, R.; Czeppe, T.; Ponomarov, O. Martensitic Transformation and Shape Memory Effect in Ni-Al Based Alloys. *MATEC Web of Conferences* 2015, *33*, 06004, doi:10.1051/matecconf/20153306004.
- 162. Wood, K.N.; Teeter, G. XPS on Li-Battery-Related Compounds: Analysis of Inorganic SEI Phases and a Methodology for Charge Correction. ACS Appl Energy Mater 2018, 1, 4493–4504, doi:10.1021/ACSAEM.8B00406.
- 163. Huang, Z.; Meng, J.; Xie, M.; Shen, Y.; Huang, Y. A Pretreatment Method to Form High-Quality LiF-Enriched Solid-Electrolyte Interfaces for Li Anode Protection in Li–O2 Batteries. J Mater Chem A Mater 2020, 8, 14198–14204, doi:10.1039/D0TA05147K.
- 164. Müller, B.R. K2CO3- and K2CO3/Porous SiO2-Doped Steam Activated Extruded Carbons Based on Multi-Component Biochar Composite: Preparation, Characterization and Kinetic Gasification Behavior. *Chemical Engineering Journal Advances* **2022**, *10*, doi:10.1016/J.CEJA.2022.100244.
- Caracciolo, L.; Madec, L.; Martinez, H. XPS Analysis of K-Based Reference Compounds to Allow Reliable Studies of Solid Electrolyte Interphase in K-Ion Batteries. ACS Appl Energy Mater 2021, 4, 11693–11699, doi:10.1021/acsaem.1c02400.
- 166. Hoque, E.; DeRose, J.A.; Kulik, G.; Hoffmann, P.; Mathieu, H.J.; Bhushan, B. Alkylphosphonate Modified Aluminum Oxide Surfaces. J Phys Chem B 2006, 110, 10855–10861, doi:10.1021/jp061327a.
- 167. Wang, X.; Liu, H.; Zhao, L.; Wang, Y.; Wang, S. Improved Resistive Switching Characteristics of Atomic Layer Deposited Al2O3/La2O3/Al2O3 Multi-Stacked Films with Al+ Implantation. *Journal of Materials Science: Materials in Electronics* 2019, 30, 12577–12583, doi:10.1007/s10854-019-01618-0.
- 168. Zähr, J.; Oswald, S.; Türpe, M.; Ullrich, H.J.; Füssel, U. Characterisation of Oxide and Hydroxide Layers on Technical Aluminum Materials Using XPS. *Vacuum* **2012**, *86*, 1216–1219, doi:10.1016/J.VACUUM.2011.04.004.
- 169. Biesinger, M.C.; Lau, L.W.M.; Gerson, A.R.; Smart, R.St.C. The Role of the Auger Parameter in XPS Studies of Nickel Metal, Halides and Oxides. *Physical Chemistry Chemical Physics* **2012**, *14*, 2434, doi:10.1039/c2cp22419d.
- 170. Biesinger, M.C.; Payne, B.P.; Grosvenor, A.P.; Lau, L.W.M.; Gerson, A.R.; Smart, R.S.C. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni. *Appl Surf Sci* 2011, 257, 2717–2730, doi:10.1016/J.APSUSC.2010.10.051.
- 171. Biesinger, M.C.; Payne, B.P.; Lau, L.W.M.; Gerson, A.; Smart, R.S.C. X-Ray Photoelectron Spectroscopic Chemical State Quantification of Mixed Nickel Metal, Oxide

and Hydroxide Systems. *Surface and Interface Analysis* **2009**, *41*, 324–332, doi:10.1002/SIA.3026.

- 172. Brisse, A.-L.; Stevens, P.; Toussaint, G.; Crosnier, O.; Brousse, T. Ni(OH)2 and NiO Based Composites: Battery Type Electrode Materials for Hybrid Supercapacitor Devices. *Materials* **2018**, *11*, 1178, doi:10.3390/ma11071178.
- 173. Freitas, M.B.J.G. Nickel Hydroxide Powder for NiO-OH/Ni(OH)2 Electrodes of the Alkaline Batteries. *J Power Sources* **2001**, *93*, 163–173, doi:10.1016/S0378-7753(00)00570-X.
- 174. Cheng, T.-L.; Lei, Y.; Chen, Y.; Fan, Y.; Abernathy, H.; Song, X.; Wen, Y.-H. Oxidation of Nickel in Solid Oxide Cells during Electrochemical Operation: Experimental Evidence, Theoretical Analysis, and an Alternative Hypothesis on the Nickel Migration. *J Power Sources* 2023, 569, 232991, doi:10.1016/j.jpowsour.2023.232991.
- 175. Biesinger, M.C. Advanced Analysis of Copper X-Ray Photoelectron Spectra. *Surface and Interface Analysis* **2017**, *49*, 1325–1334, doi:10.1002/SIA.6239.
- 176. Gan, Z.H.; Yu, G.Q.; Tay, B.K.; Tan, C.M.; Zhao, Z.W.; Fu, Y.Q. Preparation and Characterization of Copper Oxide Thin Films Deposited by Filtered Cathodic Vacuum Arc. *J Phys D Appl Phys* **2004**, *37*, 81–85, doi:10.1088/0022-3727/37/1/013.
- 177. Li, Y.H.; Chen, N.; Cui, H.T.; Wang, F. Fabrication and Characterization of Porous Ti– 10Cu Alloy for Biomedical Application. *J Alloys Compd* **2017**, *723*, 967–973, doi:10.1016/j.jallcom.2017.06.321.
- 178. Xie, F.; He, X.; Cao, S.; Mei, M.; Qu, X. Influence of Pore Characteristics on Microstructure, Mechanical Properties and Corrosion Resistance of Selective Laser Sintered Porous Ti-Mo Alloys for Biomedical Applications. *Electrochim Acta* 2013, 105, 121–129, doi:10.1016/j.electacta.2013.04.105.
- 179. Hilario, F.; Roche, V.; Jorge, A.M.; Nogueira, R.P. Application of the Transmission Line Model for Porous Electrodes to Analyse the Impedance Response of TiO2 Nanotubes in Physiological Environment. *Electrochim Acta* 2017, 253, 599–608, doi:10.1016/j.electacta.2017.09.045.
- De Levie, R. The Influence of Surface Roughness of Solid Electrodes on Electrochemical Measurements. *Electrochim Acta* 1965, *10*, 113–130, doi:10.1016/0013-4686(65)87012-8.
- 181. Guerra, C.; Sancy, M.; Walczak, M.; Martínez, C.; Ringuedé, A.; Cassir, M.; Han, J.; Ogle, K.; de Melo, H.G.; Salinas, V.; et al. Effect of Added Porosity on a Novel Porous Ti-Nb-Ta-Fe-Mn Alloy Exposed to Simulated Body Fluid. *Materials Science and Engineering C* 2020, *111*, 110758, doi:10.1016/j.msec.2020.110758.
- 182. Miki, M.; Morita, M. Evaluation of the Biocompatibility of a Ti-Ta-Sn Alloy Using Cell Cultures. *Mater Trans* **2015**, *56*, 1087–1091, doi:10.2320/matertrans.M2015062.
- 183. Tagger Green, N.; Machtei, E.E.; Horwitz, J.; Peled, M. Fracture of Dental Implants: Literature Review and Report of a Case. *Implant Dent* **2002**, *11*, 137–143, doi:10.1097/00008505-200204000-00014.
- Kumari, R.; Pfleging, W.; Besser, H.; Majumdar, J.D. Microstructure and Corrosion Behavior of Laser Induced Periodic Patterned Titanium Based Alloy. *Opt Laser Technol* 2019, *116*, 196–213, doi:10.1016/j.optlastec.2019.03.017.
- 185. Lutterotti, L.; Scardi, P. Simultaneous Structure and Size–Strain Refinement by the Rietveld Method. *J Appl Crystallogr* **1990**, *23*, 246–252, doi:10.1107/S0021889890002382.
- 186. Fakhr Nabavi, H.; Aliofkhazraei, M. Morphology, Composition and Electrochemical Properties of Bioactive-TiO2/HA on CP-Ti and Ti6Al4V Substrates Fabricated by Alkali

Treatment of Hybrid Plasma Electrolytic Oxidation Process (Estimation of Porosity from EIS Results). *Surf Coat Technol* **2019**, *375*, 266–291, doi:10.1016/j.surfcoat.2019.07.032.

- Nobial, M.; Devos, O.; Mattos, O.R.; Tribollet, B. The Nitrate Reduction Process: A Way for Increasing Interfacial PH. *Journal of Electroanalytical Chemistry* 2007, 600, 87–94, doi:10.1016/j.jelechem.2006.03.003.
- Zeng, C.L.; Wang, W.; Wu, W.T. Electrochemical-Impedance Study of the Corrosion of Ni and FeAl Intermetallic Alloy in Molten (0.62Li, 0.38K)2CO3 at 650°C. Oxidation of Metals 2000, 53, 289–302, doi:10.1023/A:1004589103992.
- 189. Trinstancho-Reyes, J.L.; Sanchez-Carrillo, M.; Sandoval-Jabalera, R.; Orozco-Carmona, V.M.; Almeraya-Calderón, F.; Chacón-Nava, J.G.; Gonzalez-Rodriguez, J.; Martínez-Villafañe, A. Electrochemical Impedance Spectroscopy Investigation of Alloy Inconel 718 in Molten Salts at High Temperature. *Int J Electrochem Sci* 2011, *6*, 419–431, doi:10.1016/S1452-3981(23)15005-X.
- 190. Spies, H.J. Corrosion Behaviour of Nitrided, Nitrocarburised and Carburised Steels. *Thermochemical Surface Engineering of Steels: Improving Materials Performance* **2015**, 267–309, doi:10.1533/9780857096524.2.267.
- 191. Yang, Y.; Wu, H. Microstructure and Microhardness of Tempered Ni–Al Alloyed Layer. *J Mater Sci Technol* **2012**, *28*, 937–940, doi:10.1016/S1005-0302(12)60154-6.
- 192. Dharmendra, C.; Gururaj, K.; Pradeep, K.G.; Mohammadi, M. Characterization of κ-Precipitates in Wire-Arc Additive Manufactured Nickel Aluminum Bronze: A Combined Transmission Kikuchi Diffraction and Atom Probe Tomography Study. *Addit Manuf* 2021, 46, 102137, doi:10.1016/j.addma.2021.102137.
- 193. Nascimento, M.S.; Santos, G.A. dos; Teram, R.; Santos, V.T. dos; Silva, M.R. da; Couto, A.A. Effects of Thermal Variables of Solidification on the Microstructure, Hardness, and Microhardness of Cu-Al-Ni-Fe Alloys. *Materials* 2019, 12, 1267, doi:10.3390/ma12081267.
- 194. Sotoodeh, K. External Topside Offshore Corrosion. In *Case Studies of Material Corrosion Prevention for Oil and Gas Valves*; Elsevier, 2022; pp. 1–96.
- 195. Leban, M.B.; Kosec, T.; Finšgar, M. Corrosion Characterization and Ion Release in SLM-Manufactured and Wrought Ti6Al4V Alloy in an Oral Environment. *Corros Sci* **2022**, 209, doi:10.1016/j.corsci.2022.110716.
- 196. Racot, A.; Aubert, I.; Touzet, M.; Thiebaut, S.; Demesy, M. Statistical Analysis of the Pitting Corrosion Induced by Potentiostatic Pulse Tests of Wrought and SLM 316L Stainless Steels. *Corros Sci* **2022**, *197*, doi:10.1016/j.corsci.2021.110036.
- 197. Fu, X.; Ji, Y.; Cheng, X.; Dong, C.; Fan, Y.; Li, X. Effect of Grain Size and Its Uniformity on Corrosion Resistance of Rolled 316L Stainless Steel by EBSD and TEM. *Mater Today Commun* **2020**, *25*, 101429, doi:10.1016/j.mtcomm.2020.101429.
- 198. Yang, G.; Du, Y.; Chen, S.; Ren, Y. Effect of Grain Size on Corrosion Behavior of 304 Stainless Steel in Coal Chemical High Salty Wastewater. *Mater Today Commun* 2023, 34, 105407, doi:10.1016/J.MTCOMM.2023.105407.
- 199. Zhai, W.; Li, J.; Zhou, R.; Sun, A.; Yan, S.; Wang, G.; Zhang, H. Improved Corrosion Resistance of Nickel-Aluminum Bronze by Electron Beam Powder Bed Fusion. *Mater Chem Phys* **2023**, 296, 127225, doi:10.1016/j.matchemphys.2022.127225.
- 200. Xu, C.; Peng, Y.; Chen, L.Y.; Zhang, T.Y.; He, S.; Wang, K.H. Corrosion Behavior of Wire-Arc Additive Manufactured and as-Cast Ni-Al Bronze in 3.5 Wt% NaCl Solution. *Corros Sci* 2023, 215, 111048, doi:10.1016/j.corsci.2023.111048.
- 201. Qin, Z.; Xia, D.H.; Zhang, Y.; Wu, Z.; Liu, L.; Lv, Y.; Liu, Y.; Hu, W. Microstructure Modification and Improving Corrosion Resistance of Laser Surface Quenched Nickel-

Aluminum Bronze Alloy. *Corros Sci* **2020**, *174*, 108744, doi:10.1016/j.corsci.2020.108744.

- 202. Wu, Z.; Cheng, Y.F.; Liu, L.; Lv, W.; Hu, W. Effect of Heat Treatment on Microstructure Evolution and Erosion-Corrosion Behavior of a Nickel-Aluminum Bronze Alloy in Chloride Solution. *Corros Sci* **2015**, *98*, 260–270, doi:10.1016/j.corsci.2015.05.037.
- 203. Murugan, V.K.; Mohanram, H.; Budanovic, M.; Latchou, A.; Webster, R.D.; Miserez, A.; Seita, M. Accelerated Corrosion of Marine-Grade Steel by a Redox-Active, Cysteine-Rich Barnacle Cement Protein. *npj Materials Degradation 2020 4:1* **2020**, *4*, 1–8, doi:10.1038/s41529-020-0124-z.
- 204. Pierre R. Roberge, P.P.Eng.F. Module Eight of CCE 281 Corrosion: Impact, Principles, and Practical Solutions Available online: https://corrosion-doctors.org/Corrosion-by-Water/Types-of-water.htm.
- 205. Totten, G.E.; MacKenzie, D.S. Handbook of Aluminum: Vol. 1: Physical Metallurgy and Processes (accessed on 4 August 2023).
- 206. Schorr, M. ASM Handbook, Volume 13c, Corrosion: Environments and Industries. Corrosion, In; 2007; Vol. 63, pp. 1–392.
- 207. Song, Q.N.; Zheng, Y.G.; Ni, D.R.; Ma, Z.Y. Studies of the Nobility of Phases Using Scanning Kelvin Probe Microscopy and Its Relationship to Corrosion Behaviour of Ni–Al Bronze in Chloride Media. *Corros Sci* **2015**, *92*, 95–103, doi:10.1016/J.CORSCI.2014.11.039.
- 208. Shen, C.; Pan, Z.; Ding, D.; Yuan, L.; Nie, N.; Wang, Y.; Luo, D.; Cuiuri, D.; van Duin, S.; Li, H. The Influence of Post-Production Heat Treatment on the Multi-Directional Properties of Nickel-Aluminum Bronze Alloy Fabricated Using Wire-Arc Additive Manufacturing Process. *Addit Manuf* 2018, 23, 411–421, doi:10.1016/j.addma.2018.08.008.
- 209. Hasan, F.; Jahanafrooz, A.; Lorimer, G.W.; Ridley, N. The Morphology, Crystallography, and Chemistry of Phases in as-Cast Nickel-Aluminum Bronze. *Metallurgical Transactions A* **1982**, *13*, 1337–1345, doi:10.1007/BF02642870.
- 210. Chen, W.; Chen, Y.; Zhang, T.; Wen, T.; Feng, X.; Yin, L. Effects of Location on the Microstructure and Mechanical Properties of Cu-8Al-2Ni-2Fe-2Mn Alloy Produced Through Wire Arc Additive Manufacturing. *J Mater Eng Perform* 2020, 29, 4733–4744, doi:10.1007/s11665-020-04955-y.
- Li, B.; Zheng, H.; Han, C.; Zhou, K. Nanotwins-Containing Microstructure and Superior Mechanical Strength of a Cu–9Al–5Fe–5Ni Alloy Additively Manufactured by Laser Metal Deposition. *Addit Manuf* 2021, *39*, 101825, doi:10.1016/j.addma.2020.101825.
- 212. Hazra, M.; Balan, K.P. Failure of a Nickel Aluminium Bronze (NAB) Canned Motor Pump Impeller Working under Polluted Sea Water – Influence of Material Selection, Section Thickness Dependent Microstructure and Temper Annealing Heat Treatment. *Eng Fail Anal* 2016, 70, 141–156, doi:10.1016/j.engfailanal.2016.07.010.
- 213. Torres Bautista, B.E.; Carvalho, M.L.; Seyeux, A.; Zanna, S.; Cristiani, P.; Tribollet, B.; Marcus, P.; Frateur, I. Effect of Protein Adsorption on the Corrosion Behavior of 70Cu-30Ni Alloy in Artificial Seawater. *Bioelectrochemistry* 2014, 97, 34–42, doi:10.1016/j.bioelechem.2013.10.004.
- 214. Lv, Y.; Guo, J.; Zhang, G.; Cao, L.; Sun, X.; Qin, Z.; Xia, D.H. Insights into the Selective Phase Corrosion of as Cast NiAl Bronze Alloy: Effect of Electrical Properties of Each Phase's Protective Film. J Alloys Compd 2022, 891, 162008, doi:10.1016/j.jallcom.2021.162008.
- 215. Yang, X.; Wu, W.; Chen, K. Investigation on the Electrochemical Evolution of the Cu-Sn-Pb Ternary Alloy Covered with CuCl in a Simulated Atmospheric Environment.

*Journal of Electroanalytical Chemistry* **2022**, *921*, 116636, doi:10.1016/j.jelechem.2022.116636.

- 216. Lebouil, S.; Tardelli, J.; Rocca, E.; Volovitch, P.; Ogle, K. Dealloying of Al2Cu, Al7Cu2Fe, and Al 2CuMg Intermetallic Phases to Form Nanoparticulate Copper Films. *Materials and Corrosion* **2014**, *65*, 416–424, doi:10.1002/MACO.201307550.
- 217. Kosari, A.; Tichelaar, F.; Visser, P.; Zandbergen, H.; Terryn, H.; Mol, J.M.C. Dealloying-Driven Local Corrosion by Intermetallic Constituent Particles and Dispersoids in Aerospace Aluminium Alloys. *Corros Sci* **2020**, *177*, 108947, doi:10.1016/j.corsci.2020.108947.
- 218. Mostafaei, A.; Zhao, C.; He, Y.; Reza Ghiaasiaan, S.; Shi, B.; Shao, S.; Shamsaei, N.; Wu, Z.; Kouraytem, N.; Sun, T.; et al. Defects and Anomalies in Powder Bed Fusion Metal Additive Manufacturing. *Curr Opin Solid State Mater Sci* 2022, 26, 100974, doi:10.1016/J.COSSMS.2021.100974.
- 219. Marattukalam, J.J.; Karlsson, D.; Pacheco, V.; Beran, P.; Wiklund, U.; Jansson, U.; Hjörvarsson, B.; Sahlberg, M. The Effect of Laser Scanning Strategies on Texture, Mechanical Properties, and Site-Specific Grain Orientation in Selective Laser Melted 316L SS. *Mater Des* **2020**, *193*, doi:10.1016/J.MATDES.2020.108852.
- 220. SONG, Q. ning; LI, H. lin; ZHANG, H. nan; HONG, H.; XU, N.; ZHANG, G. yuan; BAO, Y. feng; QIAO, Y. xin Correlation between Microstructure and Corrosion and Cavitation Erosion Behaviors of Nickel Aluminum Bronze. *Transactions of Nonferrous Metals Society of China (English Edition)* 2022, *32*, 2948–2964, doi:10.1016/S1003-6326(22)65995-8.
- 221. Zeng, Y.; Yang, F.; Chen, Z.; Guo, E.; Gao, M.; Wang, X.; Kang, H.; Wang, T. Enhancing Mechanical Properties and Corrosion Resistance of Nickel-Aluminum Bronze via Hot Rolling Process. *J Mater Sci Technol* **2021**, *61*, 186–196, doi:10.1016/j.jmst.2020.05.024.
- 222. Murray, T.; Thomas, S.; Wu, Y.; Neil, W.; Hutchinson, C. Selective Laser Melting of Nickel Aluminium Bronze. *Addit Manuf* **2020**, *33*, 101122, doi:10.1016/j.addma.2020.101122.
- 223. MOUSAVI, S.E.; NAGHSHEHKESH, N.; AMIRNEJAD, M.; SHAMMAKHI, H.; SONBOLI, A. Corrosion Performance and Tribological Behavior of Diamond-like Carbon Based Coating Applied on Ni–Al–bronze Alloy. *Transactions of Nonferrous Metals Society of China (English Edition)* **2021**, *31*, 499–511, doi:10.1016/S1003-6326(21)65512-7.
- 224. Lv, Y.; Ding, Y.; Cui, H.; Liu, G.; Wang, B.; Cao, L.; Li, L.; Qin, Z.; Lu, W. Investigation of Microscopic Residual Stress and Its Effects on Stress Corrosion Behavior of NiAl Bronze Alloy Using in Situ Neutron Diffraction/EBSD/Tensile Corrosion Experiment. *Mater Charact* 2020, *164*, 110351, doi:10.1016/j.matchar.2020.110351.
- 225. Song, Q.N.; Xu, N.; Tong, Y.; Huang, C.M.; Sun, S.Y.; Xu, C.B.; Bao, Y.F.; Jiang, Y.F.; Qiao, Y.X.; Zhu, Z.Y.; et al. Corrosion and Cavitation Erosion Behaviours of Cast Nickel Aluminium Bronze in 3.5% NaCl Solution with Different Sulphide Concentrations. *Acta Metallurgica Sinica (English Letters)* 2019, *32*, 1470–1482, doi:10.1007/s40195-019-00963-7.
- 226. Luo, Q.; Qin, Z.; Wu, Z.; Shen, B.; Liu, L.; Hu, W. The Corrosion Behavior of Ni-Cu Gradient Layer on the Nickel Aluminum-Bronze (NAB) Alloy. *Corros Sci* **2018**, *138*, 8–19, doi:10.1016/j.corsci.2018.03.050.
- 227. Sabbaghzadeh, B.; Parvizi, R.; Davoodi, A.; Moayed, M.H. Corrosion Evaluation of Multi-Pass Welded Nickel-Aluminum Bronze Alloy in 3.5% Sodium Chloride Solution: A Restorative Application of Gas Tungsten Arc Welding Process. *Mater Des* 2014, 58, 346–356, doi:10.1016/j.matdes.2014.02.019.

228. Jafari, H.R.; Davoodi, A.; Hosseinpour, S. Effect of Fluid Flow on the Corrosion Performance of As-Cast and Heat-Treated Nickel Aluminum Bronze Alloy (UNS C95800) in Saline Solution. *Corrosion and Materials Degradation 2021, Vol. 2, Pages 61-77* **2021**, *2*, 61–77, doi:10.3390/CMD2010004.