Thermally Sprayed High Temperature Sandwich Structures: Physical Properties and Mechanical Performance

by

Saeid Salavati

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Department of Mechanical and Industrial Engineering
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Abstract

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Saeid Salavati

Doctor of Philosophy
Graduate Department of Mechanical and Industrial Engineering
University of Toronto
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Metallic foam core sandwich structures have been of particular interest for engineering applications in recent decades due to their unique physical and mechanical properties. One of the potential applications of open pore metallic foam core sandwich structures is in heat exchangers. An investigation of sandwich structures fabricated from materials suitable for application at high temperatures and in corrosive environments was undertaken in this project.

A novel method for fabrication of metallic foam core sandwich structures is thermal spray deposition of the faces on the prepared surfaces of the metallic foam substrate. The objective of the current study was to optimize the twin wire arc spray process parameters for the deposition of alloy 625 faces with controllable porosity content on the nickel foam substrate, and to characterize the physical and mechanical properties of the sandwich structure.

The experimental investigations consisted of microstructural evaluation of the skin material and the foam substrate, investigation of the effect of alloying on the mechanical and thermal properties of the nickel foam, optimization of the grit-blasting and arc spray processes, observation of mechanical properties of the alloy 625 deposit by tensile testing and evaluation of the overall mechanical properties of the sandwich structure under flexural loading condition.
The optimization of arc spraying process parameters allowed deposition of alloy 625 faces with a porosity of less than 4% for heat exchanger applications. Modification of the arc spraying process by co-deposition of polyester powder enabled 20% porosity to be obtained in the deposited faces for heat shield applications with film cooling.

The effects of nickel foam alloying and heat treatment on the flexural rigidity of the sandwich structures were investigated and compared with as-received foam and as-fabricated sandwich structures. Available analytical models were employed to describe the effect of constituents’ mechanical properties on the overall mechanical performance of the sandwich structures. Finite element modeling using ANSYS Structural was used to simulate the behaviour of the sandwich structures in four-point bending. The analytical and simulation results were compared with the experimental results obtained from the flexural tests.
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# Table of Contents

Abstract........................................................................................................................................... ii
Acknowledgments................................................................................................................................. iv
Table of Contents .................................................................................................................................. v
List of Tables ......................................................................................................................................... viii
List of Figures ......................................................................................................................................... x
List of Appendices ................................................................................................................................. xv

Chapter 1 Introduction ......................................................................................................................... 1

1.1 Background and Motivation ............................................................................................................ 1
1.2 Objectives ....................................................................................................................................... 4
1.3 Guide to the thesis ........................................................................................................................... 6

References ............................................................................................................................................ 7

Chapter 2 Literature Review ................................................................................................................. 9

2.1 Sandwich structures ....................................................................................................................... 9

2.1.1 Historical background ................................................................................................................ 9
2.1.2 Concept of sandwich structures ............................................................................................... 9
2.1.3 Metallic foam core sandwich structures ............................................................................... 11
2.1.4 Mechanical properties of sandwich structures ...................................................................... 12
2.1.5 Failure modes of sandwich structures .................................................................................... 13
2.1.6 Failure map ............................................................................................................................. 15

2.2 Material selection ......................................................................................................................... 16

2.2.1 Core material ........................................................................................................................... 17
2.2.2 Facing Material ....................................................................................................................... 26
2.3 Sandwich structure fabrication processes ......................................................... 31
  2.3.1 Available methods ....................................................................................... 31
  2.3.2 Thermal spray processes ........................................................................... 32
References ............................................................................................................. 46
Chapter 3 Experimental Procedure ...................................................................... 61
  3.1 Metallic foam core ............................................................................................ 62
    3.1.1 Nickel foam ............................................................................................... 62
    3.1.2 Ni-Cr alloyed foam .................................................................................. 63
  3.2 Sandwich structure facings deposition ............................................................. 66
    3.2.1 Foam surface preparation ......................................................................... 66
    3.2.2 Arc spraying of alloy 625 ......................................................................... 69
  3.3 Characterization methods .................................................................................. 76
    3.3.1 In-flight droplet characteristics measurements ........................................ 76
    3.3.2 Microstructural characterization ............................................................... 77
    3.3.3 Thermogravimetric analysis (TGA) ........................................................ 78
    3.3.4 Mechanical tests ...................................................................................... 79
References ............................................................................................................. 84
Chapter 4 Microstructural Characterizations ......................................................... 87
  4.1 Introduction ....................................................................................................... 87
  4.2 Foam substrate .................................................................................................. 87
    4.2.1 Microstructural characterization ............................................................... 87
    4.2.2 High-temperature oxidation ..................................................................... 94
  4.3 Alloy 625 facings .............................................................................................. 95
    4.3.1 Optimization of twin wire arc spray for alloy 625 coatings ..................... 96
    4.3.2 The effect of heat treatment ..................................................................... 112
    4.3.3 Gas permeability of the alloy 625 deposits .............................................. 116
References.........................................................................................................................118

Chapter 5  Mechanical Behaviour.......................................................................................122

  5.1  Introduction.........................................................................................................................122

  5.2  Mechanical behaviour of foam ............................................................................................122
       5.2.1  Analytical model.............................................................................................................122
       5.2.2  Compression test results ...............................................................................................124

  5.3  Mechanical behaviour of facings .........................................................................................126
       5.3.1  Analytical models ...........................................................................................................126
       5.3.2  Tensile strength tests......................................................................................................129

  5.4  Mechanical performance of thermally sprayed sandwich structures ..........................132
       5.4.1  Prediction of the behaviour of sandwich panels under four-point bend loading. 133
       5.4.2  Four-point bending tests ...............................................................................................145

  5.5  Summary of the results .......................................................................................................158

References.............................................................................................................................161

Chapter 6  Closure ...................................................................................................................164

  6.1  Results and Conclusions .....................................................................................................165

  6.2  Major contributions.............................................................................................................167

  6.3  Recommendations for future work .....................................................................................168
List of Tables

Table 2-1 Some of the nickel base superalloys and their nominal chemical composition[17]..... 27
Table 2-2 Alloy 625 physical properties [17]................................................................. 29
Table 2-3 Alloy 625 important mechanical properties [72], [85]....................................... 30
Table 2-4 Common heat treatment procedures for alloy 625 [85]...................................... 31
Table 3-1 Pack chromizing powder mixture........................................................................ 64
Table 3-2 BASF Acrodur 950 L epoxy properties [2]......................................................... 67
Table 3-3 Grit blasting process parameters ...................................................................... 68
Table 3-4 External polyester powder feeder parameters- coded values.............................. 72
Table 3-5 The process factors with their levels. ................................................................. 72
Table 3-6 compositions of alloy 625 wire used as wire arc feedstock............................. 73
Table 3-7 heat treatment procedures for arc sprayed alloy 625 facings on nickel and nickel alloy foam structures ........................................................................................................... 76
Table 4-1 the concentration of Chromium on different areas of Ni-Cr foam struts .......... 91
Table 4-2 micro-harness results for Ni and Ni-Cr foam struts ......................................... 93
Table 4-3 in-flight alloy 625 droplet temperature and velocity........................................ 97
Table 4-4 EDS results; chemical composition of different point in SEM micrographs ....... 99
Table 4-5 EDS results for the spots specified in Figure 4-11 ............................................. 100
Table 4-6 experimental design matrix and the resulted coating porosity content .......... 103
Table 4-7 ANOVA for Response Surface (porosity content) Quadratic model ................. 104
Table 4-8 oxide content and hardness of alloy 625 facings deposited in different runs....... 107
Table 4-9 arc spray process parameters suggested by the model for production of dense and porous coatings with the measure microstructural properties .......................................................... 111

Table 4-10 Porosity and oxide content of the skin ................................................................. 113

Table 5-1 The properties of nickel foam structures used in this project ............................... 123

Table 5-2 Compression test results ...................................................................................... 126

Table 5-3 Elastic modulus of the coatings produced by run number 5 and run number 7
calculated by available analytical models ........................................................................... 128

Table 5-4 Mechanical properties of arc sprayed alloy 625 facings resulting from tensile test... 130

Table 5-5 Flexural rigidity of thermally sprayed metallic foam core sandwich beams prepared
with various conditions ........................................................................................................ 148
List of Figures

Figure 2-1 Schematic of the sandwich structures ................................................................. 10
Figure 2-2 different types of sandwich structures based on their core material .................... 11
Figure 2-3 Sandwich structure construction in comparison with I-beam .................................. 12
Figure 2-4 Failure modes of sandwich structures ................................................................. 14
Figure 2-5 SEM image of an open pore foam structure .......................................................... 19
Figure 2-6 application of electro-deposition technique to produce open pore Ni foam ........ 21
Figure 2-7 Open-pore nickel foams structure ...................................................................... 22
Figure 2-8 typical stress-stain curve for open pore metallic foam ......................................... 24
Figure 2-9 schematic of arc spray process (picture was produced by CACT staffs)................. 39
Figure 3-1 summary of arc spray metallic foam core sandwich structure production procedure. 62
Figure 3-2 As received 40 PPI open pore nickel foam ............................................................ 62
Figure 3-3 structural features of 10 PPI open pore nickel foam ............................................. 63
Figure 3-4 Schematic of the retort used for chromizing of the nickel foam ............................ 65
Figure 3-5 Chromizing process thermal cycle ...................................................................... 65
Figure 3-6 heat treatment procedure of chromized nickel foam............................................ 66
Figure 3-7 morphology of alloy 625 powder used for preparing temporary surface ............. 67
Figure 3-8 cross section of paste filled nickel foam a) non-grit blasted surface b) surface roughness of $R_a=18 \, \mu m$ c) $R_a=30 \, \mu m$ d) $R_a=42 \, \mu m$ ......................................................................................... 69
Figure 3-9 the geometry of Box-Behnken design. Design points are at the midpoints of edges of the design space and at the center ................................................................. 71
Figure 3-10 morphology of polyester powder particles as the pore generator agent .................. 74

Figure 3-11 Schematic of twin wire arc spraying process and external pore generator agent injector added to the process for production of porous deposits ......................................................... 75

Figure 3-12 Schematic of tensile test samples ........................................................................ 81

Figure 3-13 Schematic of tensile test equipment, front view and side view. ......................... 81

Figure 3-14 Schematic of compression test equipment .......................................................... 82

Figure 3-15 schematic of four-point bending test set up ...................................................... 83

Figure 4-1 microstructure of a) nickel foam b) Ni-Cr foam ................................................. 88

Figure 4-2 EDS map of cross section of a) as-received nickel foam b) as-chromized nickel foam c) 2 hours homogenized Ni-Cr foam d) 5 hours homogenized Ni-Cr Foam ....................... 89

Figure 4-3 linear EDS analysis for Ni-Cr foam samples a) as-chromized b) 2 hours homogenized c) 5 hours homogenized ........................................................................................................ 90

Figure 4-4 sample SEM image of 5 hours homogenized Ni-Cr foam to measure the concentration of chromium concentration in different spot of Ni-Cr foam samples ....................... 91

Figure 4-5 XRD pattern for a) as-chromized foam c) 5 hours homogenized Ni-Cr foam........ 93

Figure 4-6 plot of static air oxidation at 1000 °C for a) as-received nickel foam ....................... 94

Figure 4-7 SEM image and EDS of the surface of a Ni-Cr foam strut after hot oxidation test for 3 hours at 1000 °C showing the oxide layer on the surface of strut .................................................. 95

Figure 4-8 SEM micrograph for first layer of arc sprayed alloy 625 a) without external injection of polyester powder b) with external injection of polyester powder ........................................ 98

Figure 4-9 A typical micrograph use in EDS analysis ............................................................. 98

Figure 4-10 SEM image of typical a) alloy 625/nickel foam sandwich structure ................. 99
Figure 4-11  EDS analysis on the intermediate and light gray color areas in the SEM images of the coating cross section ................................................................. 100

Figure 4-12  XRD pattern for alloy 625 wire and as-sprayed alloy 625 coating .................. 102

Figure 4-13  a) normal probability plot for porosity content of the coating, b) predicted value of porosity versus the actual value .................................................................................................................. 105

Figure 4-14  SEM images of the coating cross section deposited produced in run number ....... 106

Figure 4-15  the perturbation plot of the response for input parameters by considering the middle level of the variables as the reference point ........................................................................................................ 108

Figure 4-16  surface plot of porosity percentage versus arc voltage and spraying distance ....... 109

Figure 4-17  surface plot of porosity percentage versus polyester powder feeding rate and arc voltage .......................................................................................................................... 109

Figure 4-18  surface plot of porosity percentage versus polyester powder feeding rate and spraying distance .......................................................................................................................... 110

Figure 4-19  Microstructure of the alloy 625 arc sprayed coating after a) 1-hour annealing, b) 3 hours annealing, c) 5 hour annealing at 900 °C ................................................................. 114

Figure 4-20  Microstructure of the alloy 625 arc sprayed coating after a) 1 hour annealing, b) 3 hours annealing, c) 5 hour annealing at 1100 °C ................................................................. 114

Figure 4-21  The XRD pattern for alloy 625 as feedstock, as-sprayed and annealed coatings .. 115

Figure 4-22  Schematic illustration of permeability test equipment .................................... 116

Figure 4-23  permeability test sample a) before mounting in the test apparatus b) after mounting in test apparatus c) during the permeability test d) during the permeability test with water on top to illustrate escape of gas .................................................................................................................. 117

Figure 5-1  Metallic foams compression test results ........................................................... 125

Figure 5-2  stress-strain curve for alloy 625 facings – dense coating (3% porosity) ............ 129
Figure 5-3 stress-strain curve for alloy 625 facings – porous coating (24% porosity) ........................................ 130

Figure 5-4 tensile test samples after the test a) as sprayed b) heat treated for 3 hours c) heat treated for 5 hours ........................................................................................................................................ 132

Figure 5-5 Geometry of a sandwich structure in 4-point bending test .............................................................. 134

Figure 5-6 Failure mode map for sandwich structures made of pure nickel foam and 24% porosity coating with the ratio of L/S=2 ........................................................................................................... 142

Figure 5-7 Failure mode map for sandwich structures made of pure nickel foam and 24% porosity coating with the ratio of L/S=3 ........................................................................................................... 142

Figure 5-8 Failure mode map for sandwich structures made of pure nickel foam and 3% porosity coating with the ratio of L/S=2 ........................................................................................................... 142

Figure 5-9 Failure mode map for sandwich structures made of pure nickel foam and 3% porosity coating with the ratio of L/S=3 ........................................................................................................... 142

Figure 5-10 Failure mode map for sandwich structures made of Ni-Cr foam and 24% porosity coating with the ratio of L/S=2 ........................................................................................................... 143

Figure 5-11 Failure mode map for sandwich structures made of Ni-Cr foam and 24% porosity coating with the ratio of L/S=3 ........................................................................................................... 143

Figure 5-12 Failure mode map for sandwich structures made of Ni-Cr foam and 3% porosity coating with the ratio of L/S=2 ........................................................................................................... 143

Figure 5-13 Failure mode map for sandwich structures made of Ni-Cr foam and 3% porosity coating with the ratio of L/S=3 ........................................................................................................... 143

Figure 5-14 Typical sandwich beam modeled in ANSYS workbench V. 15. This image captures distribution of elastic strain in the core in the linear region .................................................................................. 145

Figure 5-15 Centre point deflection for a typical thermally sprayed sandwich beam after 4-point bending load ........................................................................................................................................ 146
Figure 5-16 four-point bending load-stroke curves for a 3 hours-annealed dense arc sprayed alloy 625 coating of 1 mm thick

Figure 5-17 typical load-displacement curve for non-continuous bending test with the purpose of determining deviations from linear behavior and visual inspection

Figure 5-18 Typical load-stroke curve resulting from sample failed by core yielding mechanism a) mode A b) mode B

Figure 5-19 peak loads associated with the core yield mechanism as a function of overhang length

Figure 5-20 Typical load-stroke curve resulted from sample failed by facing indentation mechanism

Figure 5-21 peak loads associated with the indentation mechanism as a function of facings’ thickness

Figure 5-22 Typical load-stroke curve resulted from sample failed by face yielding mechanism

Figure 5-23 Peak loads associated with the face yield mechanism as a function of (L-S)

Figure 5-24 Typical load-stroke curve resulted from sample failed by face cracking mechanism

Figure 5-25 Four-point bending load-stroke curve for 500 μm-thick alloy 625 facings sandwich structure with 10 mm-thick-core of pure nickel and Ni-Cr heat treated alloyed foam

Figure 5-26 the effect of annealing on the load-stroke curve for 500 μm thick facings with 24% porosity/20 mm thick core sandwich panels

Figure 5-27 the effect of annealing on the load-stroke curve for 500 μm thick facings with 3% porosity/20 mm thick core sandwich panels
List of Appendices

Appendix A: Drawing for pack chromizing retort used for alloying the pure Ni foam ............169

Appendix B: Curing process and transformation of filling paste epoxy to high strength thermoset resin ................................................................................................................................................170

Appendix C: Arc spray process .................................................................................................................171
Appendix D: Temporary surface burnout temperature indication ..............................................................172
Appendix E: DVP-2000 system and the resulted graphs .............................................................................174
Appendix F: TGA tests on foam samples ..................................................................................................176
Appendix G: Adhesion test for arc sprayed deposits ................................................................................177
Chapter 1
Introduction

1.1 Background and Motivation

Sandwich structures are of great interest in advanced engineering applications due to their attractive properties such as high strength to weight ratio, good flexural rigidity and relatively ease of manufacture [1]–[3]. Engineering components made of sandwich structures can present the same mechanical performance as conventional ones with saving about 75% in weight, while the other specifications such as thermal insulation can be enhanced. While the technology and application of sandwich structures seem relatively new, but the concept of sandwich structure construction belongs to the mid-nineteenth century [4]. The application of sandwich structures has been the particular focus of many manufacturers in a wide variety of industries such as thermal, aviation and automobile industries due to their excellent performance.

Sandwich constructions are usually made of two faces and a thicker lightweight core. The faces and the core can be chosen from a wide variety of metallic and non-metallic materials. The faces are commonly made of stronger materials, while the core may be metallic or nonmetallic honeycombs, polymeric foams or cellular materials [5]–[8].

Traditionally, sandwich structures have been fabricated for the room temperature structural applications. While the application of sandwich structure for room temperature structures has been quite successful, optimization of these structures would extend their applications to hot temperature devices. One potential application for high-temperature sandwich structures is in heat transfer and heat insulation devices. This idea is supported by their attractive properties such as; high permeability, interconnected porosity, high surface area to volume ratio suitable for fabrication of heat-exchanger channels, and excellent thermal insulation properties across the structure thickness that is required in heat shield devices [9]. These properties along with their lower weight compared to conventional structures make sandwich structures good candidates for high-temperature applications. One of the main driving forces for optimization and commercializing high temperatures sandwich structures is the potential benefits through saving in
fuel consumption by increasing the efficiency of thermal devices and consequently a reduction in CO$_2$ emissions for fossil fuel thermal facilities [10].

The properties desired for high-temperature applications are; high resistance against hot oxidation, mechanical stability, good thermal properties, and of course reasonable fabrication cost [11]. Sandwich structures with specific thermal and physical properties in the faces and core can be designed and fabricated to serve all these criteria, while it is difficult to find conventional structures that serve all the purposes.

The sandwich structures fabricated by high temperature resistant metallic foams skinned with superalloy faces can be considered as potential replacements for the conventional heat exchanger channels and heat shield devices. The porous core would let the fluid flows through the channels and absorb or deliver the heat in such devices. Higher surface area of the foam core compared to honeycomb channels would increase the efficiency of the heat transfer device [12], [13].

Nickel base alloys and nickel superalloys are known as very good candidates for high-temperature applications where mechanical loading is combined with a hot corrosion risk [14]. A combination of strength, high corrosion resistance, high toughness and ductility, and microstructural stability at elevated temperatures is offered by nickel base superalloys [15]. While thermal conductivity of nickel is lower than some other metals such as copper and aluminum and their alloys, but the high-temperature stability of nickel and its alloys is significantly higher.

The sandwich structure faces have to be oxidation resistant and maintain their mechanical properties at an acceptable level with the ability to make a good connection with the metallic foam. Ni-base superalloys such as alloy 738, 718, 713, and 625 are widely used in high-temperature engineering applications due to their excellent high-temperature properties. Alloy 625 has shown very good hot oxidation resistance at the temperatures up to 1200 °C [16]. Therefore, it is expected that sandwich panels made of Ni-Cr alloy foam with Alloy 625 facings exhibit good corrosion resistance and mechanical properties during high-temperature operations.

Different techniques such as brazing, cladding, and diffusion bonding have been employed to place the faces on the metallic foams to fabricate metallic foam core sandwich structures. These methods are normally expensive and have problems in shaping and bonding the faces on the complex-shape foams. A new approach to fabricating metallic foam core sandwich structures is deposition of face
material on the metallic foam substrate by thermal spray processes. Thermal spray methods offer a wide range of deposits with variable thicknesses. The most common types of thermal spray methods can be listed as High Velocity Oxy Fuel (HVOF), Plasma Spray, Flame Spray and Twin Wire Arc Spray (TWAS). Amongst these, arc spray method is a cost-effective high-efficiency method suitable for mass production of engineering parts. The fundamental of this process is melting the coating material fed into the gun in the form of two individual wires by forming an electric arc at the point the wires reach together. Then, it is followed by spraying the molten droplets to the substrate using a compressed air stream passing through the gun. The droplets impact the substrate surface and make flat disks called splats. Solidification and build-up of these splats form the deposit on the substrate. The twin wire arc process parameters such as spraying voltage and gun stand-off distance can be optimized for each coating material to get maximum adhesion strength, and also control the coating porosity content [17], [18].

In the present research, twin wire arc spray process, as a rapid and cost-effective method, was used to deposit alloy 625 on nickel and Ni-Cr foam sheets. The temperature, velocity and size of the in-flight molten droplets leaving the gun towards the foam substrate were monitored in different experiments for optimization purposes. It has been shown that these characteristics are in relation with the coating mechanical and physical properties through influencing oxidation, flattening, and solidification processes of the coating splats [19]. In addition to droplet characteristics, proper bonding between deposited alloy 625 and the foam substrate as a result of surface roughening and mechanical interlocking at the interface was engineered [20]. A robot was employed for the coating depositions to keep the coating properties consistent throughout the substrate surface.

Non-permeable coating is desired for heat exchanger channel faces while the high amount of open porosity in the faces activates film cooling mechanism in heat shield devices. Porosity content of the deposited skins was controlled and optimized through systematic variation of parameters for two different applications; heat exchanger channel, and heat shield device.

Heat exchanger channels and heat shield panels are normally under bending loads. The mechanical properties of sandwich panels used in these devices are critical. However, due to the inelastic and nonlinear behavior of the constituent materials, it is difficult to analyze their mechanical behavior. In this study, mechanical behavior analysis is divided into four steps: 1- application of the analytical models to describe the elastic modulus of the alloy 625 arc sprayed coating and the
nickel foam. 2- analysis of the foam and skin mechanical properties separately through compression and tensile tests. 3- analytical investigation, and Finite Element Modeling (FEM) of the sandwich structure flexural properties by simulating four-point bending test in ANSYS. 4- Four-point bending test for the sandwich structure made in different conditions. The results of analytical and simulation studies were compared with the experimental results for validation purposes. The sandwich panels were tested in as-sprayed mode and also after heat treatment in a vacuum furnace.

Response Surface Methodology (RSM) as a powerful Design of Experiment (DOE) method was employed in conducting the surface preparation and facings deposition experiments where various parameters with different levels could possibly affect the outcome. The effect of coating microstructure, as a function of spray parameters and heat treatment, on the coating mechanical properties was studied. Failure modes of the sandwich panels were studied experimentally and compared with failure mode maps generated from analytical formulas for sandwich structures with different fabrication criteria and different architectures.

1.2 Objectives

The objective of this Ph.D. project was to fabricate metallic foam core sandwich structures by arc spray process with controllable porosity in the faces for high-temperature applications. Also, the aim of this research study was to investigate microstructural and mechanical properties of the nickel foam, alloy 625 coating, and the sandwich structures experimentally and analytically.

The following steps were taken to pursue the mentioned main objective;

- Selection of the faces and the core material based on the available knowledge and literature.

- Optimization of the surface preparation procedure to create optimum surface roughness required for mechanical bonding between the coating and filled foam substrate.

- Optimization of the twin wire arc spray process parameters for deposition of low porosity alloy 625 coatings for heat exchanger application using RSM and characterization of the low porosity coating.
• Modification of twin wire arc spray process to deposit high porosity coatings by adding polyester powder particles to the coating using an external injection nozzle, and characterization of the porous coating.

• Optimization of the pack cementation process for the production of chromium alloyed nickel foam with high oxidation resistance and characterization of the foam.

• Fabrication of the sandwich structure by deposition of alloy 625 on the nickel foam and nickel alloy foam using conventional and modified twin wire arc process.

• The use of analytical models for the foam and coating mechanical properties prediction.

• Investigation of the faces and the foam mechanical properties separately, using tensile and compression tests respectively.

• Analytical calculations of the metallic foam core sandwich structures’ stiffness.

• Finite Element Modeling (FEM) of the four-point bending test for metallic foam core sandwich beams using ANSYS software.

• Investigation of the flexural properties of the metallic foam core sandwich structures by conducting four-point bending test and identification of failure mode for the sandwich structures fabricated in various criteria.
1.3 Guide to the thesis

Chapter 2 of this thesis introduces the concept of metallic foam core sandwich structures through reviewing the relevant literature. Different fabrication methods will be described. Thermal spray methods with a focus on twin wire arc spray process will be introduced and compared. The benefits of this process compared to other available fabrication methods are highlighted in this chapter. The affecting arc spray parameters will be reviewed and compared according to the available references. The fundamentals of mechanical properties of the foam core, facings and sandwich panels are briefed in this chapter. The main failure modes of the sandwich beams will be discussed.

Chapter 3 describes the experimental procedure for fabrication of arc sprayed metallic foam core sandwich structures as well the characterization methods and procedures.

Chapter 4 reviews the microstructural characterization results towards selecting the proper foam core for high-temperature applications. Results of arc spray optimization and modification for dense and porous facings will be discussed too.

Chapter 5 focuses on the mechanical properties of the produced sandwich structure and its constituents. Analytical, FEM, and experimental studies are employed to investigate mechanical properties of the core, facings, and sandwich beams. The results are compared, and the predictions are validated for selected sandwich beam architectures. This chapter is to provide a better understanding of mechanical behavior of thermally sprayed metallic foam core sandwich structures and to summarize the failure modes of sandwich panels in failure mode maps.

Chapter 6 closes the thesis with summarizing the work done in the Ph.D. project, results of the investigations, and also suggestions for the future works in this area.
References


2.1 Sandwich structures

2.1.1 Historical background

The combination of different materials in a sandwich form was practiced by independent engineers and researchers at different times since mid-nineteenth century [1]. It has been stated by Noor et al. [2] that the concept of sandwich structures was first described by Fairbairn in 1849, who presented the experimental results for a sandwich structure made of steel sheets attached to wooden core to be employed in Robert Stephenson’s deflection-limited Britannia tubular railway bridge in North Wales [3]. The first research article about sandwich structures was published by Marguerre in 1944 [4]. Since then many researchers and engineers studied the development of sandwich structures and evaluation of their properties for different applications. These may also include advanced applications such as 3D sandwich structures for lithium-sulfur batteries [5].

2.1.2 Concept of sandwich structures

Sandwich structures, in general, are made of two faces, most often identical in thickness and material, and a low-density thicker core.

The material, architecture and manufacturing process of the core and faces are selected based on the target application that introduces a wide range of sandwich structures different in shape, material, and properties. The faces are normally made of strong materials with high stiffness such as metals, PMCs, and glass while the core is selected from low density and low stiffness materials such as metallic and non-metallic foams, honeycombs and balsa wood. These constituents are bonded together during the manufacturing process. Depending on the form of the core component, sandwich structures can be divided into four groups: foam core, honeycomb core, truss core and solid core [6]. Figure 2-1 presents the schematic of sandwich structures constituents before and
after they are bonded together. Different types of sandwich structures based on their core material are shown in Figure 2-2.

Figure 2-1 Schematic of the sandwich structures
The major applications of sandwich structures are where weight-saving is critical [7]. The main properties of sandwich structures are evaluated based on their application area. For example, in-plane properties are critical for sandwich structures employed in wind turbine blades, whereas out-of-plane compressive properties play the critical role in automotive industry [8], [9]. There are many other applications available for different types of sandwich structures, for example, NASA has employed specific types of sandwich structures in the fabrication of thermal protection systems (TPS) for the space shuttles, satellites and rocket launchers [10]. The objective of this study is to focus on the materials selection, design, and manufacturing of the high-temperature metallic foam core sandwich structures with application in the heat exchanger and heat shield devices. This type of sandwich structure is in the category of all-metal sandwich structures that both the core and facings are metallic materials.

### 2.1.3 Metallic foam core sandwich structures

The metallic foam core sandwich structures are considered as efficient components in advanced engineering applications such as aviation, marine and automotive. This is mainly because of their high specific stiffness (Young’s modulus to density ratio) and high specific strength (strength to density ratio) that make sandwich structures lighter than their counterparts [10]. The pores in a metallic foam core can be open or closed depending on the sandwich structure application [11]. The application of open pore metallic foam core sandwich structures in thermal components has
significantly grown in recent years due to their attractive properties such as interconnected porosity, high permeability and high surface to volume ratio. Recently, the application of these structure in the heat exchanger and heat shield devices has become of particular interest. This is mainly due to the unique properties of metallic foams that offer very high specific surface area (compare to honeycomb and truss structures) that can increase the efficiency of the heat exchangers [12]–[15]. Also, excellent insulation properties of the metallic foam core sandwich panels make them great candidates for the heat shield panels employed to protect industrial parts exposed to high-temperature gases.

2.1.4 Mechanical properties of sandwich structures

Sandwich structures combine two different materials in a specific architecture and scale, configured such that one forms the core and the other forms facings to provide a construction with high strength and bending stiffness at a low weight [7]. It has been shown that the mechanical behaviour of the sandwich panels is similar to the I-beams (Figure 2-3): the faces carry the bending stresses like the I-beam flanges, while the core acts similar to the I-beam web and carries shear stress and keeps the sandwich panel constituents together to form a uniformly stiffened structure. The strong adhesion between faces and the core, make the sandwich structure act as a single unit with high bending and torsional rigidity [16].

![Sandwich panel](image1)

![I-beam](image2)

**Figure 2-3 Sandwich structure construction in comparison with I-beam**
Separation of the faces with a light-weight core leads to increasing second moment of area and therefore higher bending stiffness of the material cross section (sandwich effect). The stiffness of the construction can be significantly improved by increasing the core thickness in comparison with a construction made of two faces bonded together [16]. The effect of core thickness will be studied using experimental and numerical analysis of the thermally sprayed sandwich panels in Chapter 5.

Sandwich panels are commonly subjected to bending loads in different applications where the primary loads are applied perpendicular to the faces. Some researchers have studied the sandwich structures under bending conditions and investigated the flexural properties of the sandwich panels, such as skin bending stress, flexural rigidity, and core shear stress through experimental and analytical methods [17]–[21]. The mechanical behaviour of the sandwich structures can be affected by many parameters, but the most important ones are facings and core materials’ properties, loading conditions, and architecture of the sandwich structures. The experimental procedures used for evaluation of flexural properties of the sandwich panels are 4-point or 3-point bending test, where both facings and core are considered as isotropic. In this study, the deformation and failure mechanism of the metallic foam core sandwich beams under four-point flexural loading were investigated. In four-point bending test, a long sandwich panel is subjected to a bending load normal to the plane of the sandwich panel. The centre point deflection of the beam versus the applied force is recorded in this test [22].

2.1.5 Failure modes of sandwich structures

As shown in Figure 2-4, different failure mechanisms can occur for the sandwich structures such as; bond failure or delamination of the faces, core yield (or core shear failure), tensile and compression failure of the faces (face yield), indentation of the faces into the core, face wrinkling or buckling, and face cracking [7].
Figure 2-4 Failure modes of sandwich structures
It is critical to study the failure mode of sandwich structures as a function of various architectures and materials. A better understanding of the effect of design and materials on the failure mode will help the engineers strengthening the sandwich structures. However, it is not an easy task to do stress analysis on the sandwich structures due to complex non-linear and inelastic behaviour of the components and also the boundary condition of the core and faces. Also, most of the times more than one mechanism is involved in the failure of the sandwich structures [23].

Some researchers have studied the failure modes for various types of sandwich structures. Delamination or bond failure at the interface of face and core due to low adhesion strength is very common in hybrid sandwich structures where the constituents are bonded using an adhesive. Such failure leads to loss of integrity and complete failure of sandwich structure [24]–[26]. Delamination of the face can be prevented by making stronger bonds between core and faces. Face wrinkling is not usually observed in metallic foam core sandwich structures, because the load required for this failure mode is much higher than the other failure modes [18]. Core shear failure and core indentation have been reported as common failure modes for aluminum foam core sandwich structures under bending loads [27], [28]. McCormack et al. [18] and Ashby et al. [11] presented failure models for the sandwich beams (Gibson model) and estimated the primary failure load and also the peak load for each failure mechanism, i.e. core failure, face failure (yielding), indentation of the face into the core and face wrinkling. Gibson model will be used for prediction of the dominant failure mechanism in thermally sprayed metallic foam core sandwich structures in Chapter 5 of this thesis.

2.1.6 Failure map

Sandwich structure failure mode maps can be used to design minimum-weight sandwich panels with desired mechanical strength. Failure mode maps mainly help with specifying the failure mechanism that occurs first for a given sandwich panel. The initial failure mechanism, which happens at the lowest load, depends on both constituent materials properties and architecture of the beam.

Some studies have tried to map the failure mode of sandwich panels for different types of materials and architectures. Triantafillou and Gibson [29] developed equations to describe the load at which each failure mechanism occurs for sandwich structures with rigid polyurethane foam core beams.
with aluminum faces and developed the failure map using those equations. Bart-smith et al. [30], Chen et al. [31] and Yu et al. [32], [33] reported on failure mechanism maps presenting the domain for each failure mode, and also optimized the Gibson model for cylindrical supporting and loading heads. McCormack et al. [18] tested a number of sandwich structures with aluminum foam as the core and aluminum 6061-T6 as the facings by 3-point bending setup to investigate the initial failure mode and produce the failure maps. They presented the typical displacement versus force graphs for three failure modes of these structures; core yield, indentation and face wrinkling. Chen et al [31] also tested sandwich beams made of aluminum foam and cold-worked aluminum facings using a four-point bending test setup and reported face yielding, indentation and core shear as the observed failure modes for sandwich panels.

2.2 Material selection

The room temperature application of the sandwich structures in different industries is considerable, and new applications are introduced to the market every day. While there is a big demand for the room-temperature and mid-temperature sandwich structures, optimizing them for the high-temperature applications is of particular interest of heat conversion industries. This is due to unique thermal and physical properties offered by sandwich structures for such applications. Among those, heat exchanger walls and heat shield devices are considered as the most important high-temperature applications for the metallic foam core sandwich structures. In heat exchangers, foam core can act as a permeable media capable of heat extraction from the flowing fluid and deliver it to the facings to be eventually transferred to a third media. The heat extraction efficiency of metallic foam structure is very high due to its large specific surface area. In heat shield devices, the sandwich structure can be bent or wrapped over the surfaces that are going to be protected against high-temperature gases and internally cooled by cold fluid passing through the metallic foam core. The driving force to employ a new generation of heat exchangers and heat shield devices made of metallic foam core sandwich structures is to save energy by increasing the efficiency of these devices in thermal conduction. That could eventually lead to less fossil fuel consumption and less emissions of hazardous gases. The higher efficiency of the metallic foam structures in heat exchanger applications has been reported by several researchers [12]–[15], [34]. However, there are very few studies done on the application of foam made heat exchangers and heat shield devices at temperatures of higher than 600 ºC. In this study, our focus will be on the
sandwich structures applicable in high-temperature heat exchanger and heat shield devices with the working temperatures of about 800-1000 °C.

It is critical that all the constituents of the sandwich panels stay mechanically strong and physically functional and resist chemically against the high-temperature environments. Also, bonds between the components have to be stable at high temperatures with minimum sensitivity to thermal cycles.

The criteria mentioned above suggest careful materials selection for both skin and core components as well as designing a fabrication process that satisfies the high-temperature application requirements for the bonds and interfaces.

Superalloys are known as excellent candidates for high-temperature applications. There are many different types of superalloys available that are categorized based on their base element (can be Nickel, Chromium, Iron), their alloying elements and production procedure. Nickel-base superalloys such as Inconel 625 and Inconel 718 offer very good oxidation resistant at the temperatures up to 1000 °C. These superalloys show good ductility and mechanical strength at very high temperatures [35]. One of the commercial applications for alloy 625 is in the fabrication of corrosion resistant plate heat-exchangers [36], [37]. Therefore, these alloys are considered as very good candidates for the high-temperature sandwich structure facings materials. Superalloys can also be employed as the core of such structures. However, production of superalloy foam using conventional methods is a challenge. In the next chapter of this thesis, the alloying procedure for fabrication of superalloy open pore foam structures will be presented.

2.2.1 Core material

In contrast with the conventional core materials, the use of a metallic foam core in sandwich panels can significantly reduce the weight of components required for heat shield devices and heat exchanger channels, while improving the performance in such applications simultaneously.

Nickel foams are widely used in room temperature applications because of their excellent density-compensated mechanical properties [38], [39]. Also, nickel-base alloys are used in high-temperature applications, mainly because they remain corrosion resistant, ductile, and hard enough at elevated temperatures [40]. Therefore, commercially available nickel foam is a good candidate
to be used in the core section of high-temperature sandwich structures. The high-temperature properties of the nickel foam, such as corrosion resistance and the yield strength, can be improved when it is alloyed with elements such as aluminum and chromium [41]. Nickel-aluminide alloy foams have been employed as the sandwich structure core for the applications that require high creep resistant such as turbine blades [42]. These alloys show unique mechanical behaviour by becoming fully ductile at temperatures above 1000°C [43]. For the applications such as heat-exchangers and heat shields where stresses are modest, creep resistance is less important while hot corrosion resistance is considered a crucial property. A Cr₂O₃ layer is formed on the Ni-Cr structures that protects them against further corrosion at elevated temperatures [41]. It is expected that Ni-Cr foams exhibit excellent mechanical properties along with good corrosion resistance for high-temperature applications in heat exchangers and heat shield applications.

In this section, a brief introduction to metallic foam structures and their manufacturing methods is given first, and then alloying techniques for the commercially available nickel foam structures will be reviewed.

### 2.2.1.1 Metallic Foam

Foam structures are used in many different applications from engineering to medicine. These structures also exist in nature for structural or functional purposes, such as wood and bones. Their application areas are based on their properties and include; chemical filtration, thermal insulation, acoustic insulation, heat extraction, vibration damping, and lightweight structural components [44]–[46]. The term “foam” is defined as a uniform dispersion of the gaseous phase in a liquid or solid phase [47]. The solid foam structure is sometimes called a “cellular solid”. Energy minimization limits dictate the shape of bubbles in a liquid foam. Therefore only certain morphologies can be seen in liquid foam. The same is valid for solid foams made by solidification of liquid foam. However, cellular solids are not usually made through solidification of a liquid foam. As an example, cellular metallic structures with pores of various shapes can be produced by sintering of metallic powder [48].

Foam structures can be divided into two main categories; open cell and closed cell. Pores are not interconnected in closed cell foam structures, while all pores are connected to their neighbor pores.
in an open-pore foam structure. The foam structures are usually defined by material, the number of pores per linear inch (ppi) and density.

These characteristics along with the geometry and topography of the foam structure affect its overall mechanical and physical properties. For example, in open pore foam structures, increasing the number of pores per linear inch will reduce the permeability due to greater resistance of struts against fluid flow. This, in turn, affects the performance of the structure in heat transfer applications [49]–[52]. Foam structures can be produced in a wide range of porosity content from 20% to 98%. The range of porosity achievable depends on the material, production procedure, and the process parameters during production [53], [54]. The structure of an open pore cellular material is shown in Figure 2-5.

![Figure 2-5 SEM image of an open pore foam structure](image)

The mechanical properties of the foam structures are largely determined by the mechanical properties of the struts, including their bending and buckling behaviour. It has been shown that the struts’ elastic modulus and the cell size determine the elastic modulus of the cellular material [55]. There are different methods available for production of cellular metallic materials classified in the following four categories [47], [56], [57];

a) Liquid state processing: From the liquid phase (molten metal)
b) Solid state processing: From the metallic powders

c) Vapor deposition techniques: From the vapor phase or gaseous metallic compounds

d) Electro-deposition techniques: From ionic solutions

The liquid state and solid state processing are more common for production of foams of light metals such as aluminum. Banhart [57] has summarized these production processes, which differ in the gas source, mechanism of foam stabilization, and also whether metallic powder or molten metal has been used as the initial feed.

Industrial scale production of open-pore nickel and nickel-base alloyed foams is done through either electrodeposition or vapor deposition of nickel on an open-pore polymer foam structure, as described in the following section.

### 2.2.1.2 Open pore nickel foam

The electrodeposition process for the production of open pore Ni foam is shown schematically in Figure 2-6. First, polymeric foam is made through liquid processing methods. Then, a thin conductive layer is placed on the polymeric struts through electro-less plating of an electrically conductive element, such as carbon black or graphite, on the polymer foam struts. After electrodeposition of nickel on the polymeric struts with the desired thickness, the nickel/polymer composite is thermally treated to remove the polymer from the struts’ core [47].
Figure 2-6: Application of electro-deposition technique to produce open pore Ni foam.
Open-pore nickel foam can also be produced through a vapor deposition process. In this method, nickel vapor is produced either by heating a nickel target or by decomposition of nickel carbonyl (Ni(CO)₄) in a vacuum chamber. Nickel vapor is deposited on a polymeric open-pore foam structure till the required thickness is formed on the surface of struts. The polymer is removed in the next stage through thermal or chemical treatment, and a 3D open-pore nickel foam is achieved. Hollow nickel struts form a 3D structure like what is shown in Figure 2-7.

![Figure 2-7 Open-pore nickel foams structure](image)

2.2.1.3 Mechanical properties of the foam

The mechanical properties of open cell nickel foam structures are very different from nickel in bulk forms due to the very complex architecture of foam structure, and the boundary effects of free surfaces and constrained surfaces. Consequently, some of the properties such as elastic moduli depend on the overall sample size [58]. However, these effects are not significant at a specimen size to cell size ratio of seven or larger. Open pore foam structures have open polyhedral cells made of continuous struts in a 3D interconnected network. The relative density of the metallic open pore foam structures is normally less than 0.1 (where no more than 10% of the total foam structure volume is occupied by the struts) [58]. Core strength and core elastic modulus are dependent on the foam core density relative to the bulk material. The foam mechanical properties are increased by increasing the relative density [59].
The open pore nickel foam structures used in this project are formed by a network of connected struts. The foam structures with a relative density of higher than 0.1 are known as stretch-dominant structure, while the foam structured with a relative density of less than 0.1 (less than 10% of total volume is occupied by the struts) are known as bending-dominant structures. Bending of the cell edges (struts) is the main deformation mechanism in bending-dominant foams [7]. It has been reported that for a given porosity content of open-pore foams, the effect of structural parameters such as cell shape on elastic moduli is negligible [60].

The mechanical properties of open-pore metallic foam structures are not completely isotropic. They offer a better mechanical strength and stiffness when loaded parallel to their major principal directions [61]. Collapse in open-pore foam is mainly a result of plastic hinges in the cell edges (struts) when it is subjected to the load perpendicular to its major direction. This happens when the force exceeds the elastic limit of the foam material. Collapse can occur as plastic deformation of the struts; for the foam made of plastic (ductile) materials loaded beyond their elastic limit, elastic buckling of the struts; for elastomeric foams, and brittle fracture of the struts for the brittle materials [7].

A typical stress-strain curve for open pore metallic foams in compression is observed in Figure 2-8. It can be seen that the stress-strain curve consists of three regions; 1- an elastic region where the struts are compressed elastically. The slope of the curve in this region is representative of foam elastic modulus. 2- a plastic region where the stresses in the struts are increased to beyond the yield strength of the material. 3- densification region where most of the struts have collapsed and the stress required for plastic deformation of the remaining struts is higher. [38], [59].
Elastic modulus in compression is normally smaller than elastic modulus in tension [58]. However, in this study, only compression test was done on the foam samples to extract the mechanical properties of the foam.

2.2.1.4 Nickel alloy foam

As discussed before, numerous applications have been introduced for the metallic foam structures at the ambient temperatures due to their excellent specific mechanical properties [38], [53], [62]. However, the application of metallic foams in high-temperature devices, and investigation of their properties at elevated temperatures is very limited [63]–[65]. There are many potential applications for foam structures at higher temperatures that are subject to optimization of their properties to maintain mechanical properties and withstand against hot oxidation. Nickel superalloys are known as very good candidates for high-temperature applications due to excellent oxidation resistance and mechanical properties [41].
Different fabrication methods have been employed to produce superalloy foams such as sintering of superalloy powder and vapor deposition [66], [67]. However, these processes are expensive, and shaping of the superalloy foam is a difficult task. Hodge and Dunand [68] have employed pack cementation process as a cheap and easy to do process to produce single uniform phase Ni-Al alloy foams with 28 to 33 wt% aluminum content. Alloying the nickel foam with Al and Cr through pack cementation process has been employed by Choe and Dunand [69] for the production of nickel base alloy foams with 8-9% Al or 14-18 wt% Cr and 5-9 wt% Al. As reported by them, the following heat treatment process led to the formation of $\gamma/\gamma'$ that belongs to superalloys’ microstructure.

For applications like heat exchangers where stresses are modest, creep resistance is less important than oxidation resistance. Therefore, placing a protective layer of chromium oxide (Cr$_2$O$_3$) on the foam structure is more suit to the subject of scope of this project which focuses on the heat exchanger and heat shield devices. Also, fabrication of binary Ni-Cr foam through pack cementation is easier than a ternary superalloy like Ni-Al-Cr [41].

Choe and Dunand [41] fabricated Ni-Cr foams with 9-32wt% Cr by the pack-chromizing method. It was shown in their simulations and mechanical tests that the ambient temperature compressive yield stress was increased by increasing the Cr content.

It also can be observed in Choe and Dunand’s studies [41] that the creep test results at 825 ºC illustrated a better resistance for the samples with higher Cr content. Oxidation resistant of the Ni-20 wt% Cr foam produced by Choe and Dunand [41] was reported as comparable to the bulk Ni-Cr considering the higher surface area of the foam structure. It was also resulted from their experiments that higher percentage of Cr placed on the surface of nickel alloy makes it more resistant to high-temperature oxidation.

2.2.1.5 Pack cementation process

Pack cementation is placed in the category of chemical vapor deposition (CVD) processes and has been used and improved since nearly sixty years ago. This process applies oxidation resistant and high-temperature protective coatings on the surface of parts used in the hot sections of industrial equipment like gas turbines. The most employed pack cementation processes are chromizing,
siliconizing and aluminizing. Pack cementation process consists of first preparing the powder mixture that will supply the coating material in vapor form once in the reaction temperature range and then immersing the part to be coated in a retort filled with the powder mixture. The retort will be sealed or semi-sealed and placed in a furnace with a controllable and protective atmosphere to be heated at process temperature for the required length of time to form the coating. The powder mixture consists of the coating element source powder and inert filler powder like alumina and an activator powder like the halide salts. The driving force for diffusion of the coating element(s) from the source into the substrate surface is the differences between their activities [70].

Some of the advantages of pack cementation process can be listed as followings [71]:

- The process is easy to do and easy to reproduce
- The powder mixture enables the applicator to coat complex shape components as well as holes, grooves and also open pore cellular structures
- The process is cost-effective and efficient, as many parts can be coated at the same time in a retort. The initial investment is much lower than the other vapor deposition processes such as physical vapor deposition (PVD).

2.2.2 Facing Material
2.2.2.1 Nickel alloys

As it was mentioned in section 2.2.1, all-metal sandwich structures made of nickel-base alloys can be considered as proper candidates for high-temperature application such as heat exchangers and heat shield devices. Table 2-1 shows the commercially available high-temperature nickel base alloys contain 30-70% nickel and up to 30% chromium. These alloys have face-centered cubic (FCC) structures [17], [72].
Table 2-1 Some of the nickel base superalloys and their nominal chemical composition[17]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Al</th>
<th>Ti</th>
<th>Mo</th>
<th>W</th>
<th>Nb</th>
<th>Ta</th>
<th>Fe</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel 625</td>
<td>Bal.</td>
<td>21</td>
<td>1</td>
<td>0.4</td>
<td>0.4</td>
<td>9</td>
<td>-</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>0.1</td>
</tr>
<tr>
<td>Inconel 713</td>
<td>Bal.</td>
<td>14</td>
<td>-</td>
<td>6</td>
<td>1</td>
<td>4.5</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>Bal.</td>
<td>17</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>3</td>
<td>-</td>
<td>5</td>
<td>3</td>
<td>18</td>
<td>0.06</td>
</tr>
<tr>
<td>Inconel 738</td>
<td>Bal.</td>
<td>16</td>
<td>8.3</td>
<td>3.4</td>
<td>3.5</td>
<td>1.7</td>
<td>2.6</td>
<td>0.81</td>
<td>1.7</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Inconel 738LC</td>
<td>Bal.</td>
<td>16</td>
<td>8.5</td>
<td>3.4</td>
<td>3.4</td>
<td>1.7</td>
<td>2.6</td>
<td>0.9</td>
<td>1.7</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>Inconel 100</td>
<td>Bal.</td>
<td>9.5</td>
<td>15</td>
<td>5.5</td>
<td>4.5</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>Hastalloy</td>
<td>Bal.</td>
<td>22</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>9</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>18.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Nickel base superalloys may also contain cobalt, aluminum, titanium, molybdenum, iron, tungsten, tantalum and niobium in their chemical composition. Amongst these, aluminum and titanium are responsible for the formation of γ’ phase in a two phase microstructure (γ + γ’). It is commonly believed that the high-temperature strength of these superalloys is provided by coherent γ’ phase. The amount of γ’ can be changed mainly by the aging temperature and chemical composition [73], [74]. Both γ and γ’ phases have FCC crystal structure. However, the type of atoms and their arrangement is different between these two. γ’ phase is consisting of nickel atoms at the center of faces and titanium or aluminum atoms at the corners of the cubes. The chemical formula for this phase can be written as Ni₃Ti, Ni₃Al or in general Ni₃(Al,Ti). Another phase with body-centered cubic (BCC) crystal structure called γ” can also be formed in the microstructure of Ni-base superalloys that appears as precipitates in the main phase. This phase is made by niobium with the formula of Ni₃Nb. It has been found that niobium can cause age hardening after prolonged exposure to high temperatures (around 650 °C) through precipitation of γ”. Undesirable phases such as laves, μ and σ known as tcp-type phases may also be formed in the microstructure of nickel-base superalloys that decrease mechanical properties such as ductility and rupture strength [75]–[80].

In general, Ni-Cr alloys show very good oxidation resistance. The oxidation resistance of the superalloys is provided by protective chromium oxide and aluminum oxide layers. The oxidation of nickel base superalloys can be studied in three different categories based on the composition of these alloys;
Nickel base superalloys with a chromium content of less than 10 wt%; internal \( \text{Cr}_2\text{O}_3 \) precipitates and external NiO scales are formed as a result of oxidation.

Nickel base superalloys with chromium content of 10-30 wt%; \( \text{Cr}_2\text{O}_3 \) and NiO are formed at the grain boundaries as a result of oxidation.

Nickel base superalloys with chromium content of more than 30 wt%; external \( \text{Cr}_2\text{O}_3 \) scales are formed as a result of oxidation.

However, it has been shown by some researchers that other oxides layers such as \( \text{Al}_2\text{O}_3 \), \( \text{TiO}_2 \) and NiCr\(_2\)O\(_4\) spinel can be formed in nickel base superalloys while exposed to air for a long enough time. It has been proved that the aluminum oxide layers are more resistant than chromium oxide layers at higher temperatures (around 1000 °C) and higher partial pressure of oxygen. Therefore the nickel base superalloys with both aluminum and chromium in their chemical composition are considered as important alloys for high-temperature engineering applications [17], [76], [81].

Commercial nickel base alloys such as alloy 625, alloy 718 and alloy 738 have been promoted to satisfy the needs for highly corrosion resistant alloys that survive in severe working conditions [82], [83].

Alloy 625 is a nickel base solution strengthened superalloy. It has been reported that alloy 625 shows high toughness and strength from cryogenic temperatures to 1373 °K. It is also highly resistant to Cl ion stress corrosion cracking. The high level of molybdenum and chromium in alloy 625 makes it highly resistant to chloride media such as brines and seawater. Alloy 625 has excellent fatigue strength and oxidation and corrosion resistance [84]. The strength and oxidation resistance of alloy 625 at elevated temperatures have made it an excellent candidate for high-temperature applications. Alloy 625 is widely used in aerospace industry, ammonia cracker units of heavy water plants and heat exchanger tubes and channels due to its excellent performance at higher temperatures, ease of fabrication and good weldability [74].

Alloy 625 is a good candidate for fabrication of the facings used in high-temperature metallic foam core sandwich structures because of its excellent combination of mechanical properties and corrosion resistance at high temperatures.
2.2.2.2 Physical and mechanical properties of alloy 625

Alloy 625 has been mainly designed for a combination of high oxidation resistance and mechanical strength at high-temperature applications. The mechanical strength of this alloy is provided by solution hardening effects of some alloying elements in a Ni-Cr matrix. Precipitation hardening of the alloy can be happened at high temperatures by precipitation of \( \gamma' \) and \( \gamma'' \) phases. However, this mechanism is not as significant as alloy 718. These phases are mainly made of Ti, Al, and Nb. Some other alloying elements such as columbium and molybdenum provide the excellent corrosion resistance of this alloy [85]. The important physical properties of alloy 625 are listed in Table 2-2.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (Wm(^{-1})K(^{-1}))</td>
<td>9.8</td>
</tr>
<tr>
<td>Electrical resistivity ((\mu\Omega)cm)</td>
<td>129</td>
</tr>
<tr>
<td>Specific Heat (J kg(^{-1})K(^{-1}))</td>
<td>410</td>
</tr>
<tr>
<td>Density (g/cm(^{3}))</td>
<td>8.44</td>
</tr>
<tr>
<td>Expansion Coefficient 20-100 °C (10(^{-6})K(^{-1}))</td>
<td>12.8</td>
</tr>
<tr>
<td>Melting Range (°C)</td>
<td>1280 - 1350</td>
</tr>
</tbody>
</table>

Alloy 625 exhibits very good formability and weldability. Weldability of alloy 625 is easier than many other nickel-base alloys with a high amount of alloying elements. Welded alloy 625 shows very good corrosion resistance even without post-weld heat treatment. [74].

It has been shown by Levin et al. [86] that the mechanical properties of alloy 625 are affected by strain rate and the working temperature. In their study, it has been stated that unlike the typical FCC materials, increasing the strain rate increases the yield strength. Also, the strain hardening rate is increased by decreasing the temperature or increasing the strain rate [87]. The important mechanical properties of alloy 625 are presented in Table 2-3.
### Table 2-3 Alloy 625 important mechanical properties [72], [85]

<table>
<thead>
<tr>
<th>Alloy 625</th>
<th>Poisson’s ratio (ν)</th>
<th>Elongation %</th>
<th>Elastic modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>UTS (MPa)</th>
<th>0.2% proof stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.31</td>
<td>45-50 S-A</td>
<td>205</td>
<td>78</td>
<td>810-930 S-A</td>
<td>352-520 S-A</td>
</tr>
</tbody>
</table>

S: Solution annealed at 1177 °C  
A: Annealed at 1065 °C

### 2.2.2.3 Fabrication of alloy 625 facings

Various methods have been used for fabrication of alloy 625 in different shapes. The most known methods are the continuous casting of different sections, metalworking such as forging, welding and cladding and some coating processes. Amongst fabrications methods available for fabrication and attachment of ally 625 facings on the nickel foam cores, which is the objective of this project, thermal spray is the most promising method for deposition of thick facings on complex shaped substrates with good production speed. Thermal spray methods are cost-effective solutions for the fabrication of complex shape engineering components that cannot be easily fabricated using conventional methods.

Various thermal spray methods can be employed for deposition of alloy 625 facings. These methods are mainly consisting of High Velocity Oxy Fuel (HVOF), Air Plasma Spray (APS), Vacuum Plasma Spray (VPS), Detonation Gun (DG) and Twin Wire Arc Spray (TWAS). These processes are different in heating source, feedstock form (wire for TWAS and powder for the others), carrier gas, the geometry of gun and the surrounding atmosphere (vacuum for VPS). Cost, production speed and the properties of alloy 625 deposits are varied between these methods.

During the past decade, there has been a great interest in the application of HVOF process for deposition of high-temperature corrosion resistant alloy 625 coatings onto the surface of engineering components for severe working conditions [88]–[91]. Plasma spray process has also been successfully optimized to deposit high-temperature resistant alloy 625 coatings [92]–[96]. Twin Wire Arc Spray process is a well-developed technology for deposition of thick metallic coatings up to few millimeters. Alloy 625 has been deposited by arc spray process and exhibited good quality as a high-temperature oxidation resistant coating [97], [98]
2.2.2.4 Heat treatment of alloy 625

Alloy 625 made parts are sometimes heat treated according to their fabrication method and applications. The available heat treatment processes for alloy 625 can be divided into three main categories: annealing, solution annealing, and stress relieving. Annealing heat treatment is used for recrystallization of the grains and softening of the work-hardened alloy 625 parts that are going to be employed at temperatures up to 649 ºC. If the working temperature is higher than 649 ºC, it is required to improve the high-temperature strength of the alloy through solution annealing process. The application of stress relieving process is to release residual stresses stored in the microstructure during the fabrication procedure and is usually done at the temperatures lower than annealing temperature. The common heat treatment procedures are shown in Table 2-4 [17], [85].

<table>
<thead>
<tr>
<th>Heat treatment procedure</th>
<th>Temperature (ºC)</th>
<th>Time* (min)</th>
<th>Cooling rate</th>
<th>Expected properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing</td>
<td>920-1040</td>
<td>30-60</td>
<td>Quenching in Air</td>
<td>Ambient to high temperature strength (below 1038 ºC)</td>
</tr>
<tr>
<td>Solution annealing</td>
<td>1090-1200</td>
<td>30-60</td>
<td>Quenching in Air</td>
<td>Improve strength above 816 ºC</td>
</tr>
</tbody>
</table>

* Heat treatment time is chosen according to the part volume and thickness

2.3 Sandwich structure fabrication processes

2.3.1 Available methods

As discussed in section 2.2.3.3, many methods have been employed to fabrication sandwich structures. The fabrication method depends on the skin and core materials, size and architecture of the construction, expected working conditions of the sandwich structure, and the production scale. Most of these methods follow three steps, (1) fabrication of the core, (2) fabrication of the faces
and (3) bonding the faces and core to make sandwich panels [7]. Most often the methods employed for bonding all-metal sandwich structures are high-temperature bonding processes such as brazing, welding (such as resistance welding and laser welding), and diffusion bonding [94]. Brazing and diffusion bonding are the most commonly used. Brazing consists of applying a brazing material in the form of powder, paste or a thin sheet at the interface of joining components, then heating to the reaction point of the brazing material where a liquid phase is formed and attaches the components through chemical bonding. Brazing is great for superalloys and stainless steel [99]–[101]. Diffusion bonding is a process consisting of local plastic deformation at high temperatures to attach the mating surfaces and activating inter-diffusion of the atoms across the interface. This process is useful for titanium alloys [100], [102]. However, these conventional methods have limitations in shaping and forming of the facings, especially for complex shapes [103].

A new method developed by Center for Advanced Coating Technologies (CACT) at University of Toronto for fabrication of all-metal foam core sandwich structures is thermal spraying of the faces on the metallic foam sheet. Thermal spray techniques are vital engineering processes that offer cost-effective solutions for deposition of a wide range of metallic, ceramic and polymeric materials on the complex shape substrates that cannot be easily done through conventional processes. Most common thermal spray techniques were discussed earlier in section 2.2.3.4. Arc spray process will be discussed in details, as the method employed in this research, in the next section.

2.3.2 Thermal spray processes

Fauchais et al. [104] introduce M.U. Schoop as the inventor of thermal spray who registered several patents in collaboration with others and could commercialize the process. Berndt [105] has well described the impact by Schoop on thermal spray technology. Liquid metals atomization by inert gas or high-pressure air, using metals wire and rod as the feedstock and metallic or ceramic powders have been described in Schoop’s early patents [106]–[108]. Since then many types of research and developments have been done on thermal spray processes, materials, and their applications to extend their use in various industries.

Thermal spray technology is defined as; “Thermal spraying comprises a group of coating processes in which finely divided metallic or nonmetallic materials are deposited in a molten or semi-molten condition to form a coating. The coating material may be in the form of powder, ceramic rod, wire,
or molten materials.” [104]. The cold spray cannot be included in this definition, because neither molten nor semi-molten droplets are formed in this process. However, the cold spray is considered as a thermal spray process.

All thermal spray processes consist a gun that converts the supplied energy (chemical or electrical) to the required heat for melting feedstock material. A high-velocity gas stream accelerates the molten/semi-molten droplets towards the substrate surface. The feedstock material can be in the form of powder, wire or rods [109].

Thermally sprayed coatings with a thickness of tens of micrometers to tens of millimeters are built up of layers of chemically bonded and mechanically interlocked lamellae or splats that are formed by impact, flattening, and solidification of the in-flight droplets on the substrate surface. Thermal spray coatings are commonly consisting of lamellar splats, pores, bond interfaces, oxide phases, un-melted particles, and sometimes cracks [109].

Thermal spray is considered a versatile technology in the industry that has been widely used for the production of composites of base-material/coating to provide surface resistance to corrosive, high temperature, abrasive and erosive environments while the base material does not need to be an expensive high-performance composition [110],[111].

Thermal spray processes are divided into different categories in various ways. They are first divided based on the source of energy provided to the feedstock to form molten/semi-molten droplets. A second level for dividing thermal spray processes is based on the form of feed stock material, that can be powder, wire or rod. A further division is based on the velocity of the gas stream, and finally the atmosphere of spraying. The properties of the thermal spray coatings determined by the properties of the feedstock material, thermal spray process parameters, and also the substrate specifications. Apart from feedstock material properties, maximum impact on the coating properties is by the parameters that control the droplets velocity and temperature at the impact. It has to be mentioned that different materials require different spraying conditions. Sometimes it is required to change the spraying process from one material to the other. Every thermal spray process presents some unique features that make it specifically proper for a type of coating. Five subsystems can be considered in all of the thermal spray processes that influence the coating properties [104];
1. Plume formation, controlled by spray system/gun design, gas flow rates, gas compositions, and power.

2. Feedstock, including all the properties of wire, rod or powder that is used as the coating material such as composition, size, feeder design, and positioning.

3. Spraying and deposition atmosphere, including air, vacuum, or inert gas.

4. Substrate material and specification, including oxidation state, surface roughness, and the temperature during spraying.

5. Relative motion of the spraying gun and substrate, which affects heat transfer to the substrate and coating and deposit thickness per pass.

These systems are controllable by altering the spraying process and its parameters.

Despite mentioned features, there are some other differences between thermal spray processes; namely:

- Feedstock type: the feedstock material can be in the form of wire, powder, or suspension and solution in different thermal spray processes.

- Heating source: electric arc or combustion.

- The cost of the process: The equipment, operation, and feedstock material costs are sometimes significantly different between thermal spray processes.

- The microstructure of the deposit: the porosity content, oxide content, splats shape and other microstructural features vary from one thermal spraying process to another, making them suitable for different applications, such as in membranes, wear-resistant or corrosion protection coatings.

- Heat introduced to the substrate: impact and solidification of molten droplets on the substrate surface can warm up the substrate. It can even lead to melting and re-solidification of a thin layer of the substrate. In some applications, that spray heat input can alter the
mechanical properties of the substrate in a bad way, choosing low-temperature spray methods such as arc spray and using external air cooling can be considered.

Different thermal spray processes will be discussed in the following sections.

2.3.2.1 Flame spray

Flame spray process is the simplest and among the oldest thermal spray processes. The heat source is combustion of fuel gas (C\textsubscript{x}H\textsubscript{y}) with the oxidizer (oxygen or air). Flame temperature can be controlled by controlling the composition of fuel and flow of fuel and oxidizer. The coating material is fed into the gun in wire or powder form (depending on the gun design) and carried by the hot and carrier gas to the substrate. Flame spray process works at atmosphere pressure, and the temperature and velocity of the droplet in this process are lower than other hot thermal spray processes. The flame spray system is not as complicated as the other processes, and can be moved to the working site as a portable device for on-site applications. There are many applications introduced for flame spray process such as atmospheric corrosion resistant and wear resistant coatings for low-load conditions [104], [109].

2.3.2.2 High velocity Oxy Fuel (HVOF)

This process is in fact a high velocity flame spray process [112], [113]. In HVOF process the coating material particles with a size range of 5-60 µm are injected into a high speed and high-temperature gas jet in the high-pressure combustion chamber of a specialty designed spraying gun. Combustion is done in a pressurized chamber (pressure of higher than atmospheric pressure) that is cooled by circulation of water and followed by a Laval-type nozzle. The molten or semi-molten droplets formed in this hot stream are then sprayed with a velocity of 300 to 800 ms\textsuperscript{-1} to form very dense deposits on the substrate surface [90]. The key advantage of HVOF process is achieving a high velocity of gas due to the special design of its nozzle. The velocity of gas stream exiting the nozzle is supersonics with visible diamonds shocks downstream the plume. HVOF gun is normally installed on a robot to scan the substrate and build-up a uniform coating. A low porosity coating is formed by impact, mechanical interlocking and spreading of the in-flight droplets on the substrate surface and subsequent solidification [114]. The feedstock material is commonly in the
form of powder, but special HVOF guns have been developed to use wire form feedstock [104], [109], [115]. HVOF process is capable of producing metallic, intermetallic and cermet coatings with a porosity of less than 1% and high adhesion strength. The main success of HVOF process was in the deposition of high-hardness wear-resistant tungsten carbide coatings. This process is more expensive than flame spray in investment and operation costs [116]–[118]. The microstructure of sprayed alloy 625 coating deposited by an HVOF gun was reported as a lamellar structure formed by thin layers of nickel alloy and metallic oxides [119].

2.3.2.3 Plasma spray

Plasma spray is defined as “a thermal spray process in which a non-transferred arc as a source of heat, ionizes a gas which melts the coating material, in-flight, and propels it to the workpiece” [120]. Plasma is a mixture of atoms, molecules, ions (in excited and fundamental states), electrons and photons that are electrically neutral (same number of electrons and ions). For the gases that are used in plasma spray process, thermal plasma is formed at atmospheric pressure as soon as the gas temperature reaches 7000-8000 °K. The plasma forming gases usually contain a primary gas that is responsible for flow and particle entertainment (such as N₂ or Ar) and a secondary gas that improves the gas mixture heat transfer (such as H₂ and He). The high temperature required for formation of thermal plasma is provided by a direct current arc between the anode nozzle and the cathode of the plasma spray gun. The temperature of plasma jet is usually between 8000 °K and 14000 °K at the nozzle exit. Therefore, many engineering materials including ceramics, ceramic composites, metals, intermetallics, and cermets can be sprayed and deposited as a coating on different types of substrates. This process is amongst the most expensive thermal spray processes due to high gas and electricity consumption and also initial investment [109], [111], [112]. The main application of plasma spray process is to produce thermal barrier coatings (TBCs) that are mainly made of ceramic material such as yttria-stabilized zirconia (YSZ) on hot sections of industrial equipment such as gas turbines[121], [122].

Azarmi et al. [92], [103] used APS for deposition of alloy 625 on graphite filled metallic foam substrate. The aim of their research was to produce a dense coating with a minimum amount of porosity and oxide in the microstructure. They used SG-100 plasma spray gun to spray Metco AMDRY 625 powder onto the prepared surface of nickel foam. Three different phases were
reported to be present in the lamellar microstructure of APS and HVOF sprayed alloy 625 coatings as followings:

a) The light color phase that forms the majority of the coating and has FCC structure rich in nickel. The composition of this phase was reported very close to the feedstock composition

b) Gray phase that was identified as a mixture of Ni and Cr oxides. This phase was distributed throughout the microstructure.

c) Darkest phase (black) with rounded shapes throughout the microstructure or as thin layers between the splats was recognized as the remnant porosity.

2.3.2.4 Twin wire arc spray

Twin wire arc process can be defined as: “a thermal spray process in which an arc is struck between two consumable electrodes of a coating material, compressed gas is used to atomize and propel the material to the substrate” [120].

Twin wire arc spray process is an economical method of thermal spraying that has become very popular in industrial applications due to combining low equipment and operation costs with high material deposition and energy efficiencies. Porosity content of the arc sprayed coatings is normally higher than HVOF and APS coatings. Nevertheless, in some industrial applications, higher porosity content is acceptable or even desired (such as membranes and heat shield devices [123]). Arc spray coatings are widely used for deposition of corrosion-resistant, wear-resistant, and antibacterial coatings. The applications of arc spray coatings are categorized according to different coating materials, thickness and microstructural features (i.e. porosity content, etc.) [124]–[127].

Twin wire arc spraying process

As shown in Figure 2-9, the two consumable wires which carry electrical current are continuously fed into the arc spray gun. Electric arc struck at the wire tips to provide the heat source required for melting the wire shape coating material. Molten droplets are removed by the high-pressure
cross flow of a carrier gas and sprayed towards the substrate surface. In this process, the gas is not practically heated by the electric arc, which provides lower substrate temperature during spraying compared to other processes. The temperature of electric arc can go as high as 20,000 °K, but limited to a small volume. Therefore, the wire tips are heated to temperatures above their melting point [104], [109], [128]. Unlike other thermal spray methods that the heat source is provided externally, such as combustion, the consumable wires provide a controlled arc as the source of energy for melting. The velocity of the carrier gas controls the velocity of the formed in-flight droplets which is generally few of hundreds m/s. Recently, high velocity twin wire arc spray systems have been developed for the production of dense high-strength coatings. Arc spray process has the maximum deposition efficiency and production rate amongst all the thermal spray processes. Wire arc spray system can be stationary or portable based on its application. The operation and maintenance of this process are not as complex as HVOF and APS. Twin wire arc spray coatings tend to present microstructures of similar to APS deposits with a comparable level of oxide and porosity content [129].

The commercially available wires for twin wire arc spray process in the industry are made of electrically-conductive materials, such as copper and copper alloys, stainless steel, aluminum, nickel and nickel based alloys, zinc, and Ni-Al. Recently, metal-ceramic composite coatings were prepared by using cored wires [130], [131] and pre-alloyed wires [132], [133] in which the non-conductive components are embedded inside the conductive wires as the core.
TWAS is capable of mass production of engineering components due to its higher deposition efficiency and deposition speed. The application of this process in the different industrial components has dramatically grown in recent years due to flexibility, ease of use and relatively lower material and process cost compare to other thermal spray processes. In this process, the feedstock is in the form of conductive wires made of the target coating material. The source of energy in this process is an electric arc that makes it limited to metallic feedstocks that can be formed as flexible wires [98], [134], [135].

The use of electricity as the power source, instead of flammable gases, in arc spray process and the possibility of using compressed air as the atomizing gas, makes this process safer and even more cost-efficient compared to other spray systems. Unlike the other processes, the wires are completely molten by the arc and the issues caused by partially melted particles are eliminated in this process.

In order to produce high-temperature metallic foam core sandwich structures, this research study will focus on optimization of arc spray process with controllable porosity and characterization of
the sprayed alloy 625 on metallic foam substrates. This processes will be discussed in details in the next chapter.

**In-flight droplets characteristics**

In thermal spray processes, droplets temperature and velocity are the most important and controlling factors in the behaviour of in-flight droplets and the resulting coating microstructure [136], [137]. Fauchains [111] has reviewed the studies describing the significant effect of in-flight particle velocities and temperature on splats shape and formation, specifically on flattening, solidification and oxidation that eventually affect the deposited coating microstructure and properties. In the studies carried by Friis et al. [138] it was found that microstructural variations in deposited coating may be better correlated with in-flight particle characteristics than with the operational spraying parameters.

In-flight droplet temperature depends on the feedstock characteristics such as wire size, heat capacity, and thermal conductivity. Arc spray parameters such as arc power and cross flow gas characteristics also affect the droplet temperature prior to impact. In-flight droplet velocity is related to feedstock density, and detached droplets shape, size, and mass. The droplets velocities are also affected by spraying parameters such as gas jet velocity and pressure at the exit and spraying distance. Although smaller droplets may have higher velocity compared to larger ones, their momentum is not as big as large particles. The online droplet monitoring systems have made it possible to measure the in-flight size, temperature, and velocity of the sprayed droplets before impact at any distance from the spraying gun [139]. The droplets velocity, temperature, and size distribution can be monitored and recorded as a function of position in the arc spray plume during the spray.

**Operating parameters**

The spraying parameters that can be changed and controlled in arc spray systems to alter the microstructural properties of the deposited coatings can be listed as below [131], [140]–[143]:

40
1) Feedstock (fed wires) materials: a wide range of metallic materials are used in industry including Ni superalloys, stainless steel, titanium, aluminum, copper, tin, zinc and some of their alloys. Each of these conductive materials or a combination of them as the fed wires can be used for various applications.

2) Carrier/atomizing gas: different type of gases can be used in arc spray process including dry-compressed-air, argon, and nitrogen. The carrier gas strips the molten material off the wires (atomization) and therefore needs not be flammable. Inert gases may be used to reduce the amount of oxide in the coating.

3) Carrier gas pressure: The upstream pressure of the carrier gas determines the velocity and flow rate of the gas. As discussed earlier, the gas velocity significantly affects the velocity of in-flight droplets.

4) Spray voltage: The spraying voltage defines the input power for arc struck. It indirectly affects the arc temperature and the rate at which the wires tips are melted. Spray voltage specifies the arc current in most of the arc spray systems.

5) Wire-feed-rate: Determines the rate at which consumable wires are introduced into the spraying gun, which is equivalent to the rate at which wire tips are melted.

6) Spray distance: The distance between spraying torch tip and the substrate surface. Changing the spray distance may affect the temperature of droplets at impact and amount of oxide and gain size in the ultimate microstructure.

7) Scanning speed: Defines the thickness of sprayed deposit in each pass.

**Splat formation and coating build up**

The in-flight molten droplets leaving the wires tips become spherical due to surface tension forces while traveling to the substrate surface. Droplets with given velocities and temperature of above or close to material melting temperature impact the substrate surface. Droplets compress in the axial direction and speared out perpendicular to their trajectory upon impact, and are flattened on the surface. The following rapid solidification forms the splat. In-flight droplet characteristics and
substrate specifications play a significant role in flattening and consequently final splats shapes [17], [104].

Droplet impact on the substrate and its relation with the deposited coating properties has been extensively reviewed experimentally and numerically by other researchers[144]–[147]. It has been shown that the droplet impact on the surface of the substrate may involve severe deformation with significant strain rate, recoil, splashing and rapid solidification that are significantly related to in-flight characteristics and substrate properties.

Most droplet impact studies, for modeling simplification or experimental reasons, have used smooth substrate surfaces. Key parameters for the substrate consist of surface roughness and preheating temperature. In the case of poor surface preparation, the oxide layer composition and thickness also play a considerable role [148].

Thermally sprayed coatings include billions of individual splats connected by chemical and mechanical bonding. The formation of every single splat plays a role in coating microstructure and consequently its properties. The splat solidification process is normally completed before the next molten droplet impacts the same spot. It has been claimed that flattening takes less than 5 μs after droplet impact while the solidification process is completed in 0.8-10 μs [111], [149]. Splat shape and properties depend on many parameters such as velocity, size, and thermos-physical characteristics of the in-flight droplet, as well as the substrate surface topology and properties. Disk-shaped splats may form stronger bonds together due to the elimination of pores along the splats boundaries. Flower-shaped splats that result from extensive splashing upon flattening and solidification, may form coatings with higher porosity content[17], [150].

The arc spray gun can be mounted on a robot to move horizontally and vertically across the substrate surface in a pattern chosen to uniformly cover the entire surface.

**Effect of spraying parameters on coating microstructure**

As discussed before there are many process parameters which affect the in-flight characteristics of the molten droplets, impact on the substrate, and eventually the coating microstructure and properties. Deposition of the desired microstructure requires a thorough understanding of the
correlation between spraying parameters and in-flight droplet characteristics as only then the relation between coating properties and spraying parameters can be understood. Given the temperatures and velocities ranges achievable by changing the process parameters, even small changes in arc spraying parameters can lead to considerable effects on the in-flight droplet characteristics, and consequently the coating properties.

The correlation between the coating properties and the in-flight droplet characteristic has been widely studied for HVOF [114], [151]–[155] and APS [17], [94], [156]–[158]. The analysis of in-flight droplet characteristics in wire arc sprayed coatings has not been the main focus of thermal spray technologies researchers.

**Porosity of the coating**

Porosity is one of the most important microstructural features in twin wire arc sprayed coatings. The desired percentage of porosity in the thermal sprayed coatings is designed based on their applications. For example, higher porosity content is desirable for plasma sprayed thermal barrier coatings, because the lower thermal conductivity of the air embedded inside the pores reduces the overall thermal conductivity of the coating. Very low porosity content is necessary for the corrosion resistant coatings to avoid penetration of the corrosive media into the coating/substrate interface. However, it has been proved that the density of thermal spray coatings is usually less than the bulk material. The main sources of porosity in thermal spray coatings can be listed as below [17], [119], [152], [159]:

- Splashing of the in-flight molten droplets upon impact
- Entrapment of gases between the splats
- Microporosity formed by dissolved gases
- Splat curl-up
- Embedded solid particles

The oxide phases may also cause porosity formation due to poor wetting at the time of droplet flattening that lifts the splat edges up and makes small voids. The porosity content in thermal spray
Coatings can be controlled by optimization of spraying parameters including feedstock, process parameters, distance, atmosphere, substrate properties and temperature and post-spray treatments such as annealing and laser treatment. However, changing the porosity content for twin wire arc process that consumes wire shape feedstock is only possible in a limited range [109]. The scope of current study requires both high-porosity content coatings for heat shield devices application where gas penetration through the coating cross section helps cooling the structure and dense coating for application in heat exchanger channels where sealing of the hot and cold gases are critical. New techniques will be introduced in this project to control the arc sprayed deposits porosity content via optimization of the process by response surface method and also externally added pore generator agent.

**Oxidation of the coating**

Oxide inclusions in thermally sprayed deposits are commonly observed as elongated phases that are darker in contrast with the metallic phases in the coating cross section. The interaction between the molten in-flight droplet and surrounding atmosphere (normally air) and/or heating the already deposited splats during spraying process are the main causes for oxide inclusions in the thermal spray coatings. The higher temperature of molten droplets may increase the oxide layer thickness on the in-flight droplets, producing higher content of oxides within the coating. Oxides reduce the wettability of the impacting droplets and consequently a reduction in adhesion strength between the substrate and coating. A larger concentration of oxide phase may cause poor cohesion strength between the coating splats and decrease the overall mechanical properties of the coating. In arc spray process, reducing the droplets superheat through optimization of input power and reducing substrate temperature by introducing cooling air to its surface may help reducing oxide content [131], [160].

**Substrate effect**

Formation of thermally sprayed coatings is highly affected by the substrate properties such as material, temperature, surface topography and its shape. These can affect the flattening behaviour of the splats, solidified splats morphology, porosity content, coating thickness and its uniformity,
hardness, mechanical properties and residual stresses. The higher surface roughness of substrate can increase the mechanical interlocking between the coating and substrate surface that eventually improves the coating adhesion strength. However, high surface roughness may also lead to incomplete coverage of the surface by splats and formation of a larger number of pores in the coating microstructure. Therefore coating properties can be controlled by controlling the substrate surface specifications in addition to changing the spraying parameters [161]–[163].
References


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Chapter 3
Experimental Procedure

In this chapter, the nickel foam alloying procedure for the production of Ni-Cr foam is described first. Then, the fabrication procedure for high-temperature metallic foam core sandwich structures using twin arc spray process, and the microstructural and mechanical characterization methods are explained. As discussed before, the fabrication of metallic foam core sandwich structures using twin wire arc spray process is a multi-step procedure that involves in a first step the production of a temporary surface using a curable paste upon which the in-flight molten droplets can be deposited without penetrating into the foam pores. In the second step, the temporary surface produced on the foam sheet is dried at moderate temperatures. The extra layer of the dried paste on top of struts tips is removed by machining, and the temporary surface is then roughened using grit blasting process to get the foam struts exposed. Exposed tips of the foam struts will provide the adhesion strength between coating and the foam core through mechanical interlocking. Once the desired roughness is achieved, the filler paste curing process is completed at higher temperatures to obtain high mechanical strength and high-temperature stability for the temporary surface. Finally, the faces are deposited by twin wire arc spray process followed by the burnout of the temporary surface epoxy matrix in a box furnace. Figure 3-1 summarized the arc sprayed metallic foam core sandwich structure fabrication procedure, to provide a general image of the processes that will be discussed in details in the following sections of this chapter.
3.1 Metallic foam core

3.1.1 Nickel foam

Sandwich structures examined in this study were made using both pure nickel foam and alloyed foam (Ni-Cr). The alloyed foam produced by chromizing the commercially available nickel foam sheets. Open pore 40 PPI nickel foam sheets (Yi Gong International, Jiangsu, China) with the thickness of 10 mm and 20 mm were used in this research as the core material (Figure 3-2). The employed nickel foams had a reticulated structure consisting of hollow struts, Figure 3-3.
3.1.2 Ni-Cr alloyed foam

Pack chromium cementation alloying process (chromizing) is done by the generation of halide gases. Pack chromizing has a long history of application for the bulk parts and has been well investigated. However, application of this process for open pore nickel foam may face some complications. For example, the intricate shape of the foam struts and their thin walls (around tens of µm), complex pores network and difficulties in filling the foam with cementation pack, possible two-sided diffusion in hollow struts, and extensive variation in foam struts thickness throughout the structure (normally 6 to 65 µm in a 40 PPI Ni-foam) can make the pack cementation process more complex. However, the generated gas can flow through the passages and access all the struts surfaces of the foam structure to react with nickel and deposit chromium coating. An activator is used to decrease the energy barrier against reaction between halide gases and the nickel foam. The reactions sequence during chromizing using ammonium chloride as the activator is as follows:

I. \[ \text{NH}_4\text{Cl} (s) \rightarrow \text{NH}_3 (g) + \text{HCl} (g) \]

II. \[ \text{NH}_3 (g) \rightarrow \frac{1}{2} \text{N}_2 (g) + 3/2\text{H}_2 (g) \]

III. \[ 2\text{HCl} (g) + \text{Cr(s)} \rightarrow \text{CrCl}_2 (g) + \text{H}_2 (g) \]

IV. \[ \text{CrCl}_2 (g) + \text{H}_2 (g) \rightarrow \text{Cr(s)} + 2\text{HCl} (g) \]
Formation of the chromium chloride gas is the key requirement for deposition of the chromium in the solid elemental form on nickel foam. Pack chromizing powder mixture, Table 3-1, was prepared by mixing the chromium source, activator and filler powders, according to [1].

<table>
<thead>
<tr>
<th>Powder</th>
<th>Purity (%)</th>
<th>Manufacturer</th>
<th>wt % in the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>99</td>
<td>Alfa Aesar, Ward Hill, Ma USA</td>
<td>25</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>99.9</td>
<td>Condea Vista, Ceralox</td>
<td>70</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>98+</td>
<td>Alfa AESAR</td>
<td>5</td>
</tr>
</tbody>
</table>

The powder mixture was blended using a simple hand-made low-speed low energy ball mill to get the powders particles of different materials distributed uniformly in the pack.

Pack chromizing was done on 10 mm and 20 mm thick sheets of 40 ppi open pore nickel foam in an Inconel 625 retort of 250 mm by 150 mm containing chromizing pack mixture (Figure 3-4). The foam samples were immersed in the powder mixture, and the retort was partially sealed. The retort cap was designed in a way that the air remaining in in the retort could escape by the vapor pressure of gases produced at the beginning of pack reactions. The chromizing powder to foam ratio was kept 50 gr of pack per 0.5 gr of foam throughout the experiments. An argon gas flow was fed into the furnace during the chromizing process to prevent hot oxidation of the nickel foam. Chromizing temperature regime used in this study is shown in Figure 3-5. As shown in Figure 3-5, the retort was first heated at 250 °C for 2 hours to remove any moisture from the pack and then the actual chromizing process was started by heating the retort at 1000 °C for 7 hours. The retort drawing can be seen in Appendix A.
After completion of chromizing, the cooled samples were taken out from the reacted pack and washed using ultrasonic washer/cleaner to remove the remaining partially sintered pack powder from the foam cells. Alloyed foams were then dried using high-pressure air jet. Heat treatment of chromized nickel foam sheets was done with an aim to produce uniform Ni-Cr foam. Heat treatment of alloyed foam was done in a vacuum furnace to facilitate diffusion of Cr into the strut thickness to make a uniform Ni-Cr alloy foam. The heat treatment procedure is shown in Figure 3-6.
The heating and cooling rates were chosen to be 20 °C per minute. The pressure inside the furnace during the heating, dwell time and cooling steps was $10^{-4}$ Pa.

### 3.2 Sandwich structure facings deposition

#### 3.2.1 Foam surface preparation

A paste consisting of 60 vol.% spherical alloy 625 powder (AMDRY 625 + 45–90 μm, Catalog number DSMTS-0085.6, Oerlikon Metco, Westbury, NY, USA) and 40 vol.% curable thermoplastic resin (Acrodur 950L, BASF, Mississauga, Ontario, Canada), with the properties listed in Table 3-2, was spread over and into the surface of the nickel foam sheets to make a temporary near-surface skin on both faces of the foam.

Figure 3-7 shows the morphology of alloy 625 powder used in the filler.
Table 3-2 BASF Acrodur 950 L epoxy properties [2]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy type</td>
<td>formaldehyde-free water base crosslinking acrylate resin</td>
</tr>
<tr>
<td>Crosslinking Agent</td>
<td>Polyol</td>
</tr>
<tr>
<td>Maximum storing time (months)</td>
<td>6</td>
</tr>
<tr>
<td>Solidification Temperature (°C)</td>
<td>5</td>
</tr>
<tr>
<td>Viscosity at 23 °C (mPa s)</td>
<td>900-2500</td>
</tr>
<tr>
<td>Density at 23 °C (g/cm³)</td>
<td>Approx. 1.2</td>
</tr>
<tr>
<td>pH</td>
<td>3-4</td>
</tr>
<tr>
<td>Before curing</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>After curing</td>
<td>Thermosetting, transparent</td>
</tr>
</tbody>
</table>

Figure 3-7 morphology of alloy 625 powder used for preparing temporary surface

The thickness of this paste layer was kept approximately 2 mm for all the specimens. After covering the foam surface, the paste was dried for 2 hours at 75 °C and 2 hours at 95 °C in a Despatch LAC benchtop laboratory oven to dry and stabilize the temporary surface against the grit-blasting pressure. Then, foam preparation procedure was followed by Grit-blasting of the surface to get the foam struts exposed from the dried and partially cured temporary surface. This leads to a better mechanical bonding between the foam and the skin and consequent higher adhesion strength. Grit blasting process parameters, [4].
Table 3-3, were selected based on our verified procedure to get the maximum coating density and adhesion strength. The average surface roughness (Ra, the arithmetic average of irregularities from the mean line measured within sampling length) was measured using a Precision Devices Digital Surfometer with 10 replicates for each sample in different directions. The target surface roughness, based on the experimental results published elsewhere [4], was 30 µm. SEM images of filled nickel foam before and after the grit-blasting process is shown in Figure 3-8 [4].

<table>
<thead>
<tr>
<th>parameter</th>
<th>unit</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, psi</td>
<td>psi</td>
<td>20</td>
</tr>
<tr>
<td>Blasting angle</td>
<td>degrees</td>
<td>30</td>
</tr>
<tr>
<td>Grit particles size</td>
<td>Grit size number</td>
<td>46</td>
</tr>
<tr>
<td>Blasting distance</td>
<td>mm</td>
<td>60</td>
</tr>
<tr>
<td>Number of passes</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

Curing process was then completed by heating the filled foam structure gradually in a laboratory oven at 125 and 195 °C respectively (2 hours at each temperature) for crosslinking of the epoxy molecules that finally results in transformation of epoxy to a stiff and stable thermoset that can withstand the plume gas pressure and surface temperature during spraying process. This temporary surface acts as a barrier against penetration of the in-flight droplets into the foam internal spaces during arc spraying of the alloy 625. Details of the crosslinking mechanism are presented in Appendix B.
3.2.2 Arc spraying of alloy 625

As discussed before, the aim of this study was to develop high strength oxidation resistant high-temperature metallic foam core sandwich structures for application in heat exchanger channels and heat shield devices. In addition to high mechanical strength and proper high-temperature resistance, some specific physical properties are also required for these high-temperature applications.

Heat exchanger channels facings have to be very low in porosity content resulting in no gas passage through the cross section of faces that separate hot and cold gases. It has been the aim of many studies to produce thermal spray coating with minimum porosity content and zero permeability for various applications such as corrosion resistant coatings. Several thermal spray methods have been

Figure 3-8 cross section of paste filled nickel foam a) non-grit blasted surface b) surface roughness of $R_a=18$ µm c) $R_a=30$ µm d) $R_a=42$ µm [4]
employed in our laboratory to deposit metallic facings on the metallic foams [3], [4]. The aim of all previous studies was to deposit dense facings for applications such as heat exchangers where penetration of gases through the facings is not desirable due to safety and efficiency considerations. However, another potential application of high-temperature corrosion resistant open-cell metallic foam core sandwich structures is in heat shield devices to protect critical parts from exposure to hot gases [3], [5]. In such application, cooling gas flows through the foam core to remove heat and keep the surface temperature within the desired range. The surfaces of monolithic components exposed to high-temperature gases are often protected by a boundary layer of cooler gas along the surface, typically formed by allowing cool gas to flow from internal passages through a pattern of holes drilled in the surface of the component [3], [6]. The performance of metallic foam core heat shields may be improved if the film cooling mechanism is employed in addition to internal cooling which is usually done the flow of gas through the core of the sandwich structure. However, the production of the pattern of holes by existing techniques is time consuming and expensive [3], [7]. Therefore, in addition to optimizing the arc spray process for deposition of dense alloy 625 on metallic foam structure, the feasibility of creating a sufficiently high fraction of open pores in the faces of a metallic foam core heat shield that cooling gas could pass through the faces has been explored.

Twin wire arc spray is known to be a cost-effective deposition process suitable for industrial production. The porosity content of arc sprayed deposits can be controlled by changing process parameters such as power, stand-off distance and spraying angle [3], [8],[9]. However, the range of coating porosity obtainable by these changes is limited. The addition of pore generating agents to the coating during a deposition to further increase the porosity content was investigated in this study. Hard materials have been injected into the hot gas plume downstream of the arc spray gun to produce composite wear resistant coatings that could not be fabricated using only wire feedstock material [3], [10],[11],[12]. In the present study, a similar approach was employed to incorporate polyester powder particles in the coating during deposition. The objective was to produce skins with a high percentage of open porosity by varying arc spraying process parameters, and the amount of polyester powder incorporated in the deposit. Statistical design of experiments was employed to generate the required experimental runs based on the variation of arc spraying process parameters and polyester powder feeder operating parameters. Response surface methodology (RSM) was employed to develop empirical relationships relating the parameters to the coating
porosity content. The details of the optimization procedure and experimental data can be found elsewhere [3].

3.2.2.1 Design of Experiments

A response surface methodology (RSM) based on a Box-Behnken experimental design, was employed to study the effects of arc spraying parameters and external polyester powder feeding variables on the coating porosity [13], [14]. The Box-Behnken experimental design contains the middle points of the edges of a k factor cube and includes replicated center points for orthogonality and estimation of the standard deviation [3], [15] (Figure 3-9).

![Box-Behnken Design](image)

**Figure 3-9** the geometry of Box-Behnken design. Design points are at the midpoints of edges of the design space and at the center [4].

The effects of three input factors, namely arc voltage (A), stand-off distance (B), Polyester powder feeding rate (C) at three levels were studied using Design Expert version 9 software (Stat-Ease Inc., Minneapolis, USA, http://www.statease.com). The wire feeding rate to the arc spraying gun and gun carrier gas flow rate were kept constant. The arc spraying angle for all the coatings was 90 degrees. The value of the external powder feeding rate included the feeder disk rotation rate (RPM) and feeder carrier gas flow rate (LPM) and was included as coded values in the experimental design (Table 3-4) [3]. All process parameters with their value are presented in Table 3-5.
Table 3-4 External polyester powder feeder parameters- coded values [3]

<table>
<thead>
<tr>
<th>Coded value</th>
<th>feeder disk rotation rate (RPM)</th>
<th>feeder carrier gas flow rate (LPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>+1</td>
<td>24</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 3-5 The process factors with their levels. [3]

<table>
<thead>
<tr>
<th>Factors</th>
<th>notification</th>
<th>unit</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Low (-1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Middle (0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High(+1)</td>
</tr>
<tr>
<td>Arc Voltage</td>
<td>A</td>
<td>V</td>
<td>28</td>
</tr>
<tr>
<td>Spraying Distance</td>
<td>B</td>
<td>cm</td>
<td>10</td>
</tr>
<tr>
<td>Polyester Powder Feeding rate (coded)</td>
<td>C</td>
<td>N/A</td>
<td>-1</td>
</tr>
<tr>
<td>Wire Feed Rate</td>
<td>E</td>
<td>m/min</td>
<td>7</td>
</tr>
<tr>
<td>Gun Air Flow Rate</td>
<td>F</td>
<td>SCFM</td>
<td>60</td>
</tr>
<tr>
<td>Gun Spraying Angle</td>
<td>G</td>
<td>Deg.</td>
<td>90</td>
</tr>
<tr>
<td>Gun Translation Speed</td>
<td>H</td>
<td>m/min</td>
<td>30</td>
</tr>
<tr>
<td>Gun Raster Pattern</td>
<td>I</td>
<td>pattern steps(cm)</td>
<td>Linear 4</td>
</tr>
</tbody>
</table>

Based on the combination of various levels of the input factors, 17 experimental runs, including 5 replicates of the center point, were generated by Design Expert software using the RSM/Box-Behnken method [3].

A second-order polynomial model was used to fit the response surface model to the measured porosity content. The proposed response function is presented by below expression:

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j + \epsilon
\]

Equation 3-1

where \(Y\) is the response (coating porosity content), \(\beta_0\) is the mean of the response, \(\beta_i\) represents the effect of variable \(X_i\), \(\beta_{ii}\) and \(\beta_{ij}\) are the coefficients of regression which present the effect of interactions of variables \(X_i\) and \(X_j\), and \(\epsilon\) is the random error [16].
For the three process factors, the previously mentioned polynomial model (Equation 3-1) can be written as follow:

\[
Y = \beta_0 + \beta_1(A) + \beta_2(B) + \beta_3(C) + \beta_{11}(A^2) + \beta_{22}(B^2) + \beta_{33}(C^2) + \beta_{12}(AB) + \\
\beta_{13}(AC) + \beta_{23}(BC)
\]

Equation 3-2

### 3.2.2.2 Alloy 625 feedstock

Alloy 625 wire (Metco 8625, catalog number 1001594, Oerlikon Metco, Westbury, NY, USA) with a diameter of 1.6 mm used as the arc spray feedstock for deposition of sandwich structure facings. The composition of alloy 625 wire is shown in Table 3-6.

<table>
<thead>
<tr>
<th>Element</th>
<th>Nickel</th>
<th>Chromium</th>
<th>Molybdenum</th>
<th>Niobium + Tantalum</th>
<th>Other (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>Bal.</td>
<td>21</td>
<td>9</td>
<td>4</td>
<td>NR</td>
</tr>
</tbody>
</table>

### 3.2.2.3 Pore generator agent

Spherical Shape polyester powder (Metco 600NS, +45 -125 μm, Catalog number: DSMTS-0015.3; Oerlikon Metco, Westbury, NY, USA) used as the pore generator agent to be sprayed simultaneously with the coating material to the substrate for production of porous alloy 625 coatings. The polyester powder was injected using a powder feeder and a nozzle on the surface of the substrate at the same time and same place of in-flight alloy 625 droplets impact. Morphology of the polyester powder particle is shown in Figure 3-10 [3].
3.2.2.4 Arc spray process

A twin wire arc spray system (ValuArc, Oerlikon Metco, Westbury, NY, USA) was used to produce both dense and porous alloy 626 coatings.

The process was modified by adding a powder feeder (Mettech III powder feeder, Mettech, Vancouver, Canada) with an external powder injection nozzle (internal diameter 3 mm) centered along the wire arc gun axis, to inject the pore generator agent particles into the hot gas jet at the point where the molten metal droplets reached the substrate surface. In that way, the pore agent powder particles were embedded between the deposited splats of the thermally sprayed skin before significant decomposition of the polyester occurred. The alignment and position of the nozzle were chosen to provide the most uniform distribution of the powder within the footprint of the arc sprayed metal on the substrate surface, as shown in Figure 3-11 [3], based on preliminary experiments. In the preliminary experiments, a single pass of alloy 625 was sprayed on the polished 316 stainless steel substrates (McMaster-Carr, Aurora, Canada, catalog number 88885K73) using twin wire arc operated with already optimized parameters, with and without external injection of pore generator agent [3]. It enabled studying the distribution and deposition of polyester particles in between metallic splats. Pictures of arc spray process are presented in Appendix C.

Figure 3-10 morphology of polyester powder particles as the pore generator agent [3]
3.2.2.5 Burnout process

After coating deposition, the temporary filled resin foam surface and the embedded polyester particles were removed by heating the sandwich panels to 400 °C in an atmosphere controlled furnace (Carbolite Gero chamber furnace, 30-1300 °C) at 20 °C/min, then holding for 3 hours and finally cooling to the room temperature with the same rate [3]. Details of the experimental work to find the burnout temperature can be found in Appendix D.

3.2.2.6 Heat treatment of alloy 625 deposits

Heat treatment was performed to improve the mechanical properties of as-sprayed alloy 625 facings. It has been proven that cohesion of splats (individual lamella) across their boundaries in the microstructure of thermally sprayed deposits can be enhanced through proper heat treatment processes. The heat treatment can also eliminate fine internal pores [17].

A well-chosen heat treatment can also reduce residual stresses generated during thermal spray process due to high impact energy and cooling rate of the droplets. The common heat treatment

![Figure 3-11 Schematic of twin wire arc spraying process and external pore generator agent injector added to the process for production of porous deposits [3]]
procedures for conventionally processed alloy 625 were previously presented in chapter 2. The main reason to anneal the sandwich panels is to improve as-sprayed alloy 625 mechanical properties, but extra care must be taken at the same time to avoid any damage to the foam core. It has been shown by other researchers in our laboratory that heat treatment at 1100 °C provides the best results for the strengthening of the coating [18]. In this study, heat treatment of the as-sprayed samples was done at 900 and 1100 °C in different dwell time hours in a high-temperature vacuum furnace (Vac-Aero, Canada). The mechanical properties of each sample were investigated through the tensile test of the facings and flexural test of the whole sandwich panel to find the best heat treatment procedure. Heat treatment procedures used in this study are listed in Table 3-7. The heating/cooling rate for all the experiments was constant, 20 °C/min.

<table>
<thead>
<tr>
<th>HT Temperature (°C)</th>
<th>HT Dwell Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Sprayed</td>
<td>0</td>
</tr>
<tr>
<td>900</td>
<td>1</td>
</tr>
<tr>
<td>900</td>
<td>3</td>
</tr>
<tr>
<td>900</td>
<td>5</td>
</tr>
<tr>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td>1100</td>
<td>3</td>
</tr>
<tr>
<td>1100</td>
<td>5</td>
</tr>
</tbody>
</table>

3.3 Characterization methods

3.3.1 In-flight droplet characteristics measurements

As discussed in Chapter 2, information about the size, temperature, and velocity of the in-flight droplets contribute to a better understanding of the relation between arc spray process parameters and the deposited coating microstructural properties. The online droplet monitoring systems have enabled researchers to measure the in-flight droplets characteristics at any distance from the spraying gun to the substrate surface. The in-flight droplet properties were measured for all different spraying runs prior to deposition on the foam substrates using a DPV-2000 (Tecnar Automation Ltee, QC, Canada) monitoring system. The DPV-2000 monitoring equipment consists of a sensing head connected to a detection module by an optical cable. The detection module
transfers the data to a computerized controlling system where the measured droplets characteristics are shown online during the spray.

The mechanism of measuring droplets velocity is based on the determination of the time of flight between the two slits optical photomask on the sensing head. The droplet temperature is measured using two-color pyrometry theory. Before each run, at each spraying distance, the DVP-2000 sensing head was aligned and auto-centered according to the spraying gun axis in both the vertical and horizontal directions. Spraying runs were performed for droplets characteristics measurements, without placing a substrate in front of the plume.

The DPV-2000 equipment employed in this project and some of its resulted graphs for arc sprayed alloy 625 have been shown in Appendix E.

3.3.2 Microstructural characterization

Microstructural characterizations of foam substrates, alloy 625 wire and arc sprayed coating were performed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), (first SEM instrument: Hitachi Scanning Electron Microscope SU3500 with Oxford X-Max 80 mm², second SEM instrument: table-top TM3000, Hitachi High-Technologies Canada Incorporated, Toronto, ON). The etching solution used for Ni-Cr foams was consisting of 100 ml HNO₃ and 10 ml HF, and the etching solution used for pure nickel foam was consisting of 3 ml HF and 80 ml HNO₃ according to the literature [19]. Grain size for the foam samples was calculated by drawing 10 random lines on each micrograph and following ASTM E112-96 standard [20].

A Java-based image analysis software, ImageJ (http://imagej.nih.gov/ij/), was employed to quantify the porosity content of different coatings [21]. Image analysis (IA) has been established as a reliable technique for characterization of porosity in thermal spray coatings, with an uncertainty of approximately 2% [22], [23]. The alloy 625 facing samples were cross-sectioned using a diamond blade before the microscopy and microhardness tests. Samples were mounted in a vacuum chamber to allow complete filling of the foam pores, and polished by 320-1200 grit SiC papers followed by 9, 3, and 1 um diamond-impregnated disks in an automatic polishing machine (EcoMet 250 Pro Grinder-Polisher with AutoMet 250 Power Head, Buehler, Whitby, ON,
Canada). At least 10 equally spaced SEM images of 1024 by 768 pixels were taken from the prepared cross sections of each sample in the secondary electron (SE) and backscattered electron (BE) imaging modes for accurate differentiation between the existing phases. The magnification (500×), illumination conditions and field of view were kept constant [3].

X-ray diffractometry (XRD) was performed using Rigaku MiniFlex 600 with Cu Kα radiation (X= 1.542 A) at 40 kV and a scanning rate of 1.45 degree/min. For phase analysis of the samples.

In addition to the microstructural characterization of the foam structures, the theoretical (ideal) density of each type of foam was estimated using the below equation [18];

\[ \rho_{\text{ideal}} = \sum V_i \rho_i \]  
Equation 3-3

Where \( V_i \) is volume fraction of the major different phases that form the foam structure, and \( \rho_i \) is the density of those phases. The main phases can be identified from XRD test results. Fraction of each phase was determined by image analysis of 5 SEM micrographs using ImageJ software.

The density of the block shape samples was calculated using the below equation;

\[ \rho_{\text{apparent}} = \sum \frac{\text{Sample weight}}{(a \times b \times c)} \]  
Equation 3-4

Where a, b and c are the length, width and height of the block shape samples.

Having the \( \rho_{\text{apparent}} \) and \( \rho_{\text{ideal}} \) in hand, we are able to calculate the fraction porosity of the nickel foam structures using the below equation [24];

\[ F_P = \frac{\rho_{\text{ideal}} - \rho_{\text{apparent}}}{\rho_{\text{ideal}}} \]  
Equation 3-5

3.3.3 Thermogravimetric analysis (TGA)

The high-temperature oxidation behavior of Ni and Ni-Cr foams and the arc sprayed alloy 625 coatings (as-sprayed and annealed) was tested using a SETSYS Evolution TGA instrument in an air atmosphere. TGA analysis was conducted based on an isothermal mass gain method during the high-temperature air exposure period in the chamber of the TGA test machine. Small samples of
about 50 mg in weight were cut from each type of foam based on the operations manual of the instrument. After ultrasonic washing in water and raising in ethanol, each sample was completely dried and placed in a small cylindrical alumina crucibles attached to the TGA machine and tested individually. An air flow rate of 0.1 l/min was running through the chamber for all the experiments while the temperature was kept 1000 °C throughout the test, for 3 hours. The heating rate to reach the static temperature was 20 °C /min for all the experiments. The TGA test temperature was chosen according to the maximum temperature that had been monitored on the surface of the previously developed foam heat exchangers and heat shields, reported between 900 to 1000 °C. The cooling fluids circulated in the heat shield and heat exchanger devices do not let the temperature goes higher than the mentioned range.

The weights of the samples and crucibles were measured precisely before and after the TGA test at room temperature and repeated for three times. Changes in mass of the foam samples were also monitored online during the TGA test. The difference between initial and final weight indicates the amount of oxygen gained by the sample to form the oxide. Pictures of the instrument and some resulted graphs can be seen in Appendix F. The weight gain was normalized by original sample weight for plotting the TG graphs.

### 3.3.4 Mechanical tests

In this study, the mechanical behavior of the facings and foam were investigated individually in aim to have a better understanding of mechanical properties of metallic foam core sandwich structures. The elastic modulus of alloy 625 facings was investigated using uniaxial tensile test, and the effect of arc spray and heat treatment process parameters were studied. Mechanical properties of the Ni and Ni-Cr foams were examined through uniaxial compression test. The overall mechanical performance of sandwich structures was measured by the four-point bending test.

#### 3.3.4.1 Microhardness

A Vickers micro-hardness testing machine (Zwick micro-hardness machine) was employed to measure the hardness of foam struts and alloy 625 coatings on their cross section. The foam
samples were tested under applied load of 100 grams for 15 seconds, and alloy 625 samples were tested under 1000 grams for 25 seconds. Five replicates were done for each sample by considering enough space between the indentations to avoid the work-hardening effects on micro-hardness test results. For the coating samples, the long axis of the indent was parallel to the coating surface in all the experiments.

3.3.4.2 Facings tensile test

The mechanical properties of facings produced with different sets of twin wire arc spray process parameters were examined using tensile test. Sub-size samples were used for this purpose because of the size limitations. Tensile test specimens were cut by electrical discharge machining (EDM) from arc sprayed alloy 625 facings of 500 micrometers in thickness deposited on foam substrates. Samples were made perpendicular to spraying direction according to ASTM E8/E8M-10 [25]. The cut samples were slightly ground on the back sides to remove the remaining foam struts and other asperities such as sintered metallic powder in filling paste. Schematic of the sub-size tensile test specimen along with facings splat orientation is shown in Figure 3-12. Tensile tests were done using a precise tensile test machine (Table-Top Universal / Tensile Tester SHIMADZU EZ-L, Japan) at a displacement rate of 1 mm/min. Tensile load and cross head displacement were measured to produce stress-stain curves. The tests were stopped once the samples failed. The schematic of tensile test machine is shown in Figure 3-13. Tests were repeated 5 times for each type of samples. The average of elastic modulus and yield point found for each type of sample plus the deviation from average will be reported in Chapter 5.
Figure 3-12 Schematic of tensile test samples

Figure 3-13 Schematic of tensile test equipment, front view and side view.
3.3.4.3 Foam compression test

As received nickel foam and Ni-Cr foam were tested using uniaxial compression test by an Autograph AG-I Universal tester, 50 kN, Shimadzu machine to investigate their mechanical properties and deformation mechanism.

Compression test samples were cut from the nickel and Ni-Cr foam sheets to a cube of 20 mm in edges using a diamond blade. Top Face displacement rate of 1 mm/min was kept constant in all the compression experiments. The compression tests were stopped once the third stage of typical metallic foam compression test (increase in load due to foam densification) was observed in apparent stress versus stain diagram. Schematic of compression test setup is shown in Figure 3-14.

Tests were repeated five times for each type of samples. The elastic moduli and yield strength measured for the foam samples will be presented in chapter five.

![Figure 3-14 Schematic of compression test equipment](image-url)
3.3.4.4 Four-point bending test

The flexural rigidity of the thermally sprayed metallic foam core sandwich structures was measured using four-point bending test. Sandwich beams of 25 mm in width and 66, 70, 90, 100 mm in length were cut out of the coated foam sheets of 10 and 20 mm in thickness, according to specific size ratios given in the ASTM C 393-00 standard [26]. The four-point bending test apparatus was mounted on a universal testing machine (Autograph AG-I Universal tester, 50 kN, Shimadzu). The distance between loading rollers (S) and supporting rollers was 20 and 40 to 60 mm, respectively. During the tests, the applied force was recorded continuously while the crosshead moved at a constant rate of 1 mm/min. Each test was ended at the point of the first major load drop. The schematic of four-point bending test can be seen in Figure 3-15. Tests were repeated three times for each type of sandwich panel. The average of flexural rigidity measured for each type of sandwich panels plus the deviation from average will be reported in the next chapter.

![Figure 3-15 schematic of four-point bending test set up](image)
References


Chapter 4
Microstructural Characterizations

4.1 Introduction

This chapter presents the results of the microstructural characterizations techniques described in chapter 3. At first, as received nickel foam is compared with chromized nickel foam samples in the microstructure, hardness, and oxidation resistant. Then, the effect of various processing parameters on the porosity content, oxide content and hardness of arc sprayed alloy 625 skin is investigated, and the optimum spraying conditions for different application are identified using design of experiment (DOE) methods.

4.2 Foam substrate

As received and chromized foam substrates were investigated using different characterization methods introduced in Chapter 3 to study their chemical composition, available phases, microstructural uniformity, high-temperature oxidation resistance and mechanical performance.

4.2.1 Microstructural characterization

SEM micrographs of the surface of foam samples were used to observe the grains morphology and to measure the grain size within the microstructure of foam struts. The microstructure of as-received nickel foam and as-chromized Ni-Cr foam on the surface of their struts are shown in Figure 4-1 a and Figure 4-1 b, respectively. Grains in both types of foam substrates are relatively equiaxed. The grain size for as-received nickel foam and as-chromized Ni-Cr foam were 24±10 µm and 18±15 µm, respectively.
The nickel foam chromizing processes followed by the homogenizing process at 1200 °C for 2 and 5 hours to get the chromium layer diffused into the struts’ wall thickness and make a uniform Ni-Cr alloy. The EDS maps of foam strut cross section for an as-received nickel foam, an as-chromized nickel foam, 2 hours homogenized Ni-Cr foam and 5 hours homogenized Ni-Cr foam samples are shown in Figure 4-2 a to d, respectively. A sharp visual gradient of Cr concentration on the struts’ surface is visible for as-chromized foam samples, while the distribution of Cr is more uniform in the homogenized samples. In the as-chromized foam sample, the concentration of chromium is higher on the struts’ surface compared to their thickness. It could provide higher oxidation resistant, but may not significantly improve the mechanical properties of the foam [1], [2]. The annealing process moves the chromium atoms from the surfaces towards the core of struts. Driving force for such diffusion is Cr concentration gradient across the struts’ wall thickness.

Figure 4-1 microstructure of a) nickel foam b) Ni-Cr foam
Although it has been stated by other researchers [1] that homogenizing time of 48 hours is required to get a chemically uniform Ni-Cr foam, it can be seen in EDS maps (Figure 4-2) that after 5 hours
the Ni-Cr foam seems to be almost uniform in Cr distribution. The EDS linear analysis for the as-chromized, 2 hours annealed and 5 hours annealed Ni-Cr foam samples are shown in Figure 4-3 a to c, respectively. In all the cases, graphs demonstrate that the concentration of chromium on the struts’ outer faces remains higher than other parts of the foam struts; that increases the possibility of getting a continuous Cr₂O₃ on the surface. In general, a higher concentration of Cr on the surface can help the formation of protective Cr₂O₃ layers during operation, and consequently a better oxidation resistance, that is of interest of this research [1], [3].

Quantitative result of EDS analysis obtained from the foam samples confirms the total concentration of around 20 percent Cr for the chromized foams. That is in agreement with the graph Choe and Dunand [1] developed to show the effect of chromizing time on the Cr concentration at 1000 °C. However, the Cr content varies across the strut’s wall thickness. EDS spot analysis was performed on the cross section of alloyed foam struts before and after homogenizing. Three spots were chosen on the cross section of foam struts to capture the Cr concentration gradient through the wall thickness. Table 4-1 summarizes the chromium content on different places of Ni-Cr alloyed foam samples. Figure 4-4 shows a sample of analyzed SEM image.
Table 4-1 the concentration of Chromium on different areas of Ni-Cr foam struts

<table>
<thead>
<tr>
<th></th>
<th>strut’s outer surface</th>
<th>mid plane</th>
<th>Strut’s inner surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-chromized Ni-Cr foam</td>
<td>36 ± 0.2</td>
<td>4 ± 0.2</td>
<td>12 ± 0.2</td>
</tr>
<tr>
<td>2 hours homogenized Ni-Cr foam</td>
<td>25 ± 0.2</td>
<td>12 ± 0.2</td>
<td>19 ± 0.2</td>
</tr>
<tr>
<td>5 hours homogenized Ni-Cr foam</td>
<td>21 ± 0.3</td>
<td>16 ± 0.1</td>
<td>18 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 4-4 sample SEM image of 5 hours homogenized Ni-Cr foam to measure the concentration of chromium concentration in different spot of Ni-Cr foam samples
The struts’ grain size after 2-hour homogenizing was 26±15 µm, and after 5 hours of homogenizing was 31±12 µm. EDS spot analysis confirmed variation in composition by the distance from the surface. It suggests a multi-phase structure for the chromized foam structure. Similar results were reported by Hodge et al. for nickel aluminide foams produced by pack aluminization of open-pore nickel foam [4]. Based on these results, 5 hours homogenizing can produce a uniform enough foam for applications require higher mechanical properties for the foam structures. However, the main purpose of foam alloying practice, in this study, was to improve the high-temperature oxidation resistant of the foam for heat exchanger and heat shield applications. Chromium rich layers on the surface are considered as protective skins for nickel struts [1]. Therefore, further in foams’ characteristics investigations, the oxidation resistance and mechanical properties of the as-received and Ni-Cr foams were tested and compared to choose the best candidate for high-temperature applications.

The XRD patterns of foam samples are shown in Figure 4-5. As received foam XRD pattern shows only pure nickel peaks, while peaks for Cr and Cr₂O₃ are present in the Ni-Cr foams XRD patterns. It can be seen the Cr peaks are very sharp for the as-chromized sample while they are weak for the annealed samples. This is because in annealed foam Cr diffuses into the thickness of the foam struts that is not accessible for the employed x-ray, and on the other hand the Cr atoms make Ni-base alloys and are not present as an individual phase.

The results of microhardness test conducted at the cross section of different foams are presented in Table 4-2. The indenter was placed at the center of struts wall thickness for all the samples for consistency of the test method and the resulted data. As expected, based on solid solution strengthening concept, the hardness of the struts increases with Cr content. The measured hardness values of the annealed samples are higher than the one obtained for the as-chromized sample. The reason is that hardness test was conducted on centre spots far enough from the struts’ surface, that Cr had not the chance of reaching there in the as-chromized sample. That illustrates the importance of homogenizing to improve the mechanical properties of foam struts by the formation of Ni-Cr solid solution.
Table 4-2 micro-harness results for Ni and Ni-Cr foam struts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micro-hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Foam</td>
<td>72 ± 3</td>
</tr>
<tr>
<td>As chromized foam</td>
<td>91 ± 14</td>
</tr>
<tr>
<td>Ni-Cr 2 hour annealed foam</td>
<td>122 ± 12</td>
</tr>
<tr>
<td>Ni-Cr 5 hour annealed foam</td>
<td>131 ± 11</td>
</tr>
</tbody>
</table>

Figure 4-5 XRD pattern for a) as-chromized foam c) 5 hours homogenized Ni-Cr foam c) as-received Ni foam
4.2.2 High-temperature oxidation

The kinetics of mass gain for different types of foam structures (as received foam and alloyed foams) during the TG tests conducted for 3 hours at 1000 °C are shown in Figure 4-6 Error! Reference source not found. It is clearly seen that the oxidation kinetics of pure nickel foam is significantly slowed by chromizing. The as-chromized foam shows a better oxidation resistant than the annealed foams due to a thicker layer of Cr-rich deposit on the surface of struts that can rapidly form Cr$_2$O$_3$ protective scale and significantly reduce oxidation rate of the foam structure. The NiO oxide layer that is formed on the surface of pure Ni foam is porous and cannot act as a protective layer, while the Cr$_2$O$_3$ oxide layer formed on the Ni-Cr alloys is dense and coherent.[1], [5]–[7].

The high-temperature oxidation resistant of the metallic components depends on the formation and properties of the exposed surfaces’ scales that act as a barrier to oxygen diffusion into the deeper areas. As it can be seen in Figure 4-7, the formed scale on the Ni-Cr foam is a dense protective layer of oxide formed on the surface of the foam after 3 hours at 1000 °C in air. Possible oxide
phases that can be formed in such alloy are NiO, Cr₂O₃, and NiCr₂O₄ depending on oxidation regime and temperature [5]. However, the formation of Cr₂O₃ at the oxidation temperatures of above 800 ºC becomes dominant [8]. Based on the TGA test results, the oxidation kinetics of homogenized foam samples (2 hours and 5 hours annealed Ni-Cr foams) are very similar. The initial rate of oxidation for the 5 hours annealed Ni-Cr foam is higher than the 2 hours annealed Ni-Cr foam, but the difference is negligible. Results suggest that the hot oxidation behavior of the as-chromized and homogenized alloyed foam samples are acceptable, compare to pure Ni foam, and the decision to choose the proper one should be made based on the mechanical properties of them.

4.3 Alloy 625 facings

Twin wire arc spray process was employed for the production of alloy 625 facings using alloy 625 wires. The optimization of arc spray process was conducted using DOE methods for production of dense and porous coatings applicable in heat exchanger channels and heat shield devices, respectively.

The grit-blasting process parameters for preparation of a surface capable of making good mechanical interlocks with the arc spray deposit were studied and optimized using DOE methods before optimization of Arc spray process. That was actually due to the importance of adhesion strength between the facings and the core of sandwich structures to avoid any delamination and

<table>
<thead>
<tr>
<th>Element</th>
<th>AN Series</th>
<th>C norm. [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>28 K-series</td>
<td>9339  60.84</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8 K-series</td>
<td>5644  18.02</td>
</tr>
<tr>
<td>Chromium</td>
<td>24 K-series</td>
<td>3400  21.14</td>
</tr>
</tbody>
</table>

Figure 4-7 SEM image and EDS of the surface of a Ni-Cr foam strut after hot oxidation test for 3 hours at 1000 ºC showing the oxide layer on the surface of strut
interface failure. The adhesion test procedure is described and results are presented in Appendix G.

The variable arc spray operating parameters are limited, and also have to be chosen in a short specific range suitable for arc stability. However, further changes in coating characteristics can be performed externally by changing the stand-off distance or adding the desired components to the solidifying coating, externally [9]. In this study, the arc spray operating parameters, stand-off distance, and the external polyester powder feeding rate were considered as the process parameters for optimization purposes. Our aim was to enable arc spray process, as a cost-efficient and fast production technique, for the production of dense and porous alloy 625 faces with high adhesion strength for high-temperature applications. The following sections will describe the results of the experimental procedure followed to reach this goal.

4.3.1 Optimization of twin wire arc spray for alloy 625 coatings

4.3.1.1 In-flight droplet characteristics

Spraying voltage and stand-off distance (spraying distance) are the parameters that could vary and affect the in-flight characteristics of the arc spray system available in our laboratories. The spraying amperage is changed mainly as a function of voltage variations in a Metco Value Arc machine. To study the in-flight characteristic of the sprayed droplets, first set of deposition experiments were performed by changing one parameter at a time while keeping the other parameters constant at their middle value (distance = 150 mm and voltage= 32 V). The effects of arc spray parameters on the in-flight alloy 625 droplets velocity, size and the temperature are shown in Table 4-3. It can be seen that the maximum traveling velocity is at the distance of 150 mm from the gun. The temperature of the droplets is decreased by around 100 °C as a function of stand-off distance, while still significantly above alloy 625 melting point. Therefore, the effect of stand-off distance on the droplets temperature is negligible for each spraying velocity. The size of droplets increases by increasing the stand-off distance that could be due to joining the small droplets to the bigger ones on their flight path towards the substrate surface.

Changing the arc voltage has a greater effect on the temperature of in-flight droplets, while does not change their velocity significantly. The higher the arc voltage, the higher the droplets average
temperature. It is also observed that the droplets average size is decreased by increasing the arc voltage that could be due to stronger arc, which can break up the just formed droplets before escaping the gun. The information obtained from the DPV 200 tests will be used to correlate the coating properties with the spraying parameters in the following section.

<table>
<thead>
<tr>
<th>Run</th>
<th>Arc voltage (V)</th>
<th>Spraying distance (mm)</th>
<th>Droplet velocity (m/sec)</th>
<th>Droplet temperature (°C)</th>
<th>Droplet size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32</td>
<td>100</td>
<td>158 ± 35</td>
<td>2534 ± 163</td>
<td>30 ± 16</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>150</td>
<td>161 ± 31</td>
<td>2498 ± 147</td>
<td>34 ± 16</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>200</td>
<td>152 ± 24</td>
<td>2456 ± 163</td>
<td>36 ± 16</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>150</td>
<td>160 ± 30</td>
<td>2386 ± 159</td>
<td>35 ± 16</td>
</tr>
<tr>
<td>5</td>
<td>36</td>
<td>150</td>
<td>163 ± 36</td>
<td>2655 ± 170</td>
<td>32 ± 16</td>
</tr>
</tbody>
</table>

### 4.3.1.2 Coating formation

To study the coating formation and the behavior of polyester powder particles at impact, only one pass of alloy 625 was deposited on stainless steel coupons by the rapid movement of the coupons in front of the in operation gun and external injector of the polyester powder.

Examples of the deposits formed in the preliminary experiments by a single pass of the torch are shown in Figure 4-8. For the sample shown in Figure 4-8-a, there was no injection of polyester powder, while the sample shown in Figure 4-8-b was deposited by maximum possible polyester powder injection rate. EDS analyses of the chemical composition of the areas outlined in Figure 4-9 are shown in Table 4-4 [10]. From these results the dark spots (P) can be identified as polyester particles, the lighter color (C) areas as alloy 625 splats, and the very light grey (S) areas as the stainless steel substrate. The polyester powder particles are not burnt-out at the time of deposition, but are embedded in between the alloy 625 splats. The injection of the polyester particles just before droplets impact limits the exposure of the particles to high-temperature and therefore minimizes the amount of decomposition [10].
By counting the polyester particles deposited in a specific surface area using image analysis (ImageJ, http://imagej.nih.gov/ij/) and comparing that for different injection configurations, a nozzle to substrate distance of 60 mm and an angle of 60° were found to be the most effective position and angle of the nozzle yielding maximum number of polyester powder particles uniformly distributed over the substrate surface [10].

![Figure 4-8 SEM micrograph for first layer of arc sprayed alloy 625 a) without external injection of polyester powder b) with external injection of polyester powder][10]

![Figure 4-9 A typical micrograph use in EDS analysis][10]
Table 4-4 EDS results; chemical composition of different point in SEM micrographs

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Iron</th>
<th>Nickel</th>
<th>Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point C</td>
<td>9.45</td>
<td>10.10</td>
<td>3.98</td>
<td>Balance</td>
<td>22.21</td>
</tr>
<tr>
<td>Point P</td>
<td>Balance</td>
<td>18.46</td>
<td>6.06</td>
<td>6.46</td>
<td>9.36</td>
</tr>
<tr>
<td>Point S</td>
<td>0.6</td>
<td>1.10</td>
<td>Balance</td>
<td>7.82</td>
<td>23.70</td>
</tr>
</tbody>
</table>

4.3.1.3 First set of facing deposition experiments

For a better understanding of the arc sprayed alloy 625 deposits on the foam substrates, a set of coatings were deposited with the parameters suggested by our lab manager. These deposited were used only to ensure the capability of the process in fabricating sandwich structures, and also for general microstructural observations.

SEM images of a typical arc sprayed alloy 625 coating on foam substrate is shown in Figure 4-10-a. Figure 4-10-b shows a higher magnification image of the coating microstructure. The foam struts are partially embedded in the arc sprayed deposit that provides the required adhesion strength to the sandwich panels. The coating topology is copied from the grit-blasted surface of the foam that contains hill shape asperities on top of the strut tips, and a flat surface in the areas between them.

Figure 4-10 SEM image of typical a) alloy 625/nickel foam sandwich structure  
b) arc sprayed alloy 625 microstructure
Three different levels of contrast are observed in Figure 4-10-b. As discussed before, the darkest phase (black spots) is representative of the pores formed inside the coating microstructure. Further characterization techniques were used to determine the phases available in the deposited alloy 624 coatings. EDS analysis was employed to investigate the chemical composition of different color phases in the coating microstructure. Figure 4-11 shows an example of EDS results for the tested samples. The average composition of each phase (differentiated by the contrast in SEM images) in the presented coating microstructure is shown in Table 4-5.

![Figure 4-11](image)

**Figure 4-11** EDS analysis on the intermediate and light gray color areas in the SEM images of the coating cross section

<table>
<thead>
<tr>
<th></th>
<th>Ni wt%</th>
<th>Cr wt%</th>
<th>Mo wt%</th>
<th>Nb wt%</th>
<th>Fe wt%</th>
<th>O wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot A</td>
<td>76 ± 2</td>
<td>12 ± 1</td>
<td>7 ± 2</td>
<td>3 ± 1</td>
<td>0.5 ± 0.3</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>Spot B</td>
<td>18 ± 1.5</td>
<td>56 ± 2</td>
<td>6 ± 2</td>
<td>5 ± 2</td>
<td>0.5 ± 0.3</td>
<td>14 ± 1.5</td>
</tr>
<tr>
<td>Spot C</td>
<td>64 ± 2</td>
<td>20 ± 1</td>
<td>5 ± 2</td>
<td>9 ± 2</td>
<td>0.5 ± 0.2</td>
<td>1.5 ± 0.7</td>
</tr>
</tbody>
</table>

Errors and deviations automatically calculated by the SEM software

The high amount of oxide in the intermediate color phase is related to the oxides formed on the surface of flying droplets during their travel from the spraying gun to the substrate surface, as a result of interaction with surrounding atmosphere. It has been observed that the oxide content is
increased by increasing the spraying distance. This oxide phase has also been observed in alloy 625 coatings sprayed by APS and HVOF processes [10], [11]

The XRD pattern for the alloy 625 wire feedstock and as-sprayed alloy 625 coating are shown in Figure 4-12. It can be seen that the microstructure of the alloy 625 has been changed significantly during the arc spray deposition process, and sharp chromium oxide peaks have appeared in the pattern. These results, along with the EDS results presented in Table 4-4 suggest that the moderate gray phase is rich in chromium oxide. The oxide phase is formed on the surface of in-flight droplets and thus in most of the cases is solidified in between the splats to make a network of a continuous and thin layer of oxide inside the microstructure. Such distribution of oxides can significantly reduce the mechanical properties of thermal spray coatings [10], [12].
4.3.1.4 The spraying runs

As described in our published paper [10], a response surface methodology (RSM) based on a Box-Behnken experimental design, was employed to study the effects of arc spraying parameters and external polyester powder feeding variables on the coating porosity content [10]. Optimization of the process for minimum oxide content was not the aim of this optimization work, as the priority was to get dense and porous permeable coatings. However, the intent was to minimize the oxide content through the proper post-spray heat treatment process that will be discussed in the next sections.
Table 4-6 presents the summary of experimental runs and resulted porosity content in the alloy 625 deposits.

Table 4-6 experimental design matrix and the resulted coating porosity content [10]

<table>
<thead>
<tr>
<th>Run</th>
<th>Arc Voltage (V)</th>
<th>Spraying Distance (mm)</th>
<th>Polyester Powder Feeding Rate (coded*)</th>
<th>Coating Porosity Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>Response</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>36</td>
<td>20</td>
<td>0</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>15</td>
<td>0</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>15</td>
<td>0</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>20</td>
<td>0</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>28</td>
<td>15</td>
<td>1</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>36</td>
<td>10</td>
<td>0</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>7</td>
<td>36</td>
<td>15</td>
<td>-1</td>
<td>5 ± 0.5</td>
</tr>
<tr>
<td>8</td>
<td>32</td>
<td>10</td>
<td>1</td>
<td>16 ± 3</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10</td>
<td>-1</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>10</td>
<td>28</td>
<td>10</td>
<td>0</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>11</td>
<td>32</td>
<td>15</td>
<td>0</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>12</td>
<td>32</td>
<td>15</td>
<td>0</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>13</td>
<td>32</td>
<td>20</td>
<td>1</td>
<td>15 ± 3</td>
</tr>
<tr>
<td>14</td>
<td>36</td>
<td>15</td>
<td>1</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>15</td>
<td>32</td>
<td>15</td>
<td>0</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>16</td>
<td>28</td>
<td>15</td>
<td>-1</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>17</td>
<td>32</td>
<td>20</td>
<td>-1</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>

*Coded values for external polyester powder feeding rate:

<table>
<thead>
<tr>
<th>Coded value</th>
<th>Feeder disk rotation rate (RPM)</th>
<th>Feeder carrier gas flow rate (LPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>+1</td>
<td>24</td>
<td>26</td>
</tr>
</tbody>
</table>

A polynomial model was fit to the porosity measurements with coefficients significant at a 95% confidence level using the Box-Behnken/RSM method. The resulting empirical relationship between the coded values of the input factors and the porosity is [10]:

\[
\text{Porosity} = 9.10 - 0.92(A) + 0.18(B) + 6.08(C) - 3.24(A^2) - 0.66(C^2) - 0.42(AB) - 0.43(AC)
\]

Equation 4-1
The larger the coefficient, the more significant the effect of that parameter on the porosity. The most significant factor affecting the coating porosity content was the external powder feeding rate.

**Adequacy of model**

Analysis of variance (ANOVA) was employed to study the adequacy of the developed model [13]. ANOVA results for the response, coating porosity content, are presented in Table 4-7 [10].

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>349.85</td>
<td>9</td>
<td>38.87</td>
<td>367.71</td>
<td>&lt; 0.0001</td>
<td>significant</td>
</tr>
<tr>
<td>A-Arc Voltage</td>
<td>6.84</td>
<td>1</td>
<td>6.84</td>
<td>64.75</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>B-Spraying Distance</td>
<td>0.25</td>
<td>1</td>
<td>0.25</td>
<td>2.32</td>
<td>0.1717</td>
<td></td>
</tr>
<tr>
<td>C-Polyester powder injection rate</td>
<td>295.25</td>
<td>1</td>
<td>295.25</td>
<td>2792.86</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>0.72</td>
<td>1</td>
<td>0.72</td>
<td>6.83</td>
<td>0.0347</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>0.72</td>
<td>1</td>
<td>0.72</td>
<td>6.83</td>
<td>0.0347</td>
<td></td>
</tr>
<tr>
<td>BC</td>
<td>0.30</td>
<td>1</td>
<td>0.30</td>
<td>2.86</td>
<td>0.1346</td>
<td></td>
</tr>
<tr>
<td>A^2</td>
<td>44.13</td>
<td>1</td>
<td>44.13</td>
<td>417.47</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>B^2</td>
<td>0.24</td>
<td>1</td>
<td>0.24</td>
<td>2.25</td>
<td>0.1776</td>
<td></td>
</tr>
<tr>
<td>C^2</td>
<td>1.85</td>
<td>1</td>
<td>1.85</td>
<td>17.48</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>0.74</td>
<td>7</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>0.48</td>
<td>3</td>
<td>0.16</td>
<td>2.46</td>
<td>0.2023</td>
<td>not significant</td>
</tr>
<tr>
<td>Pure Error</td>
<td>0.26</td>
<td>4</td>
<td>0.065</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>350.59</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>10.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C.V. %</td>
<td>3.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRESS</td>
<td>8.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-Squared</td>
<td>0.9979</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adj R-Squared</td>
<td>0.9952</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pred R-Squared</td>
<td>0.9769</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adeq Precision</td>
<td>66.568</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The model $P$-values (probability of error) were calculated to verify the significance of the empirical relationships. In general, $P$-values of more than 0.05 is identified as ‘non-contributing’ or ‘not significant’ [10].
Using the $F$-values ($F$-value indicates if a group of variables is jointly significant), the significance of the coefficient of each of the terms in the model could be assessed [10], [14]. The coefficients for all the individual factors except B (Spraying Distance) were significant. The B term was retained in the model because of the significance of the AB term. The coefficient for the interaction of B and C was not significant, nor was that for $B^2$. The significance of the model is shown by the $P$-value of less than 0.0001. The adequacy of the model was further supported by a lack of fit $P$-value of 0.2023, which is insignificant [10], [15]. The determination coefficient (R-squared) is near 1.000, and the coefficient of variation (CV%) is small, indicating that the quality of the fit of the model is good.

The normal probability plot is shown in Figure 4-13a. It can be seen that the residuals fall on a straight line, indicating that the errors are normally distributed [10], [16]. Figure 4-13 b shows the plot of predicted value versus actual value. The predicted values are in good agreement with the actual values, confirming the adequacy of the model [10].

![Figure 4-13 a) normal probability plot for porosity content of the coating, b) predicted value of porosity versus the actual value [10]](image)

SEM images of alloy 625 coating cross sections sprayed in different spraying runs (Table 4-6) are shown in Figure 4-14. The porosity content of the arc sprayed deposit varies between the runs, significantly. The morphology and size of the holes (pores) in Figure 4-14 c and d suggest that the
polyester powder burnout has left a pore in these coatings' microstructure. Therefore, the pores are bigger than natural thermal spray coatings’ pores. The pores in the coatings prepared without external injection of the pore generator agent are small and distributed across the coating. Also, it can be observed that the amount of oxide phase is different for these samples. The coating sprayed by high arc voltage (run 6) exhibits a large area of moderate gray phase, Cr-rich oxide. That confirms the effect of higher voltage on droplets temperature increase and consequent higher oxidation rate.

![SEM images of the coating cross section deposited produced in run number a) 9 b) 16 C) 6 and d) 5](image)

The hardness of alloy 625 facings deposited by different spraying runs is presented in Table 4-8. It can be seen that the coatings with higher amount of oxide phase have a higher hardness.
Table 4-8 oxide content and hardness of alloy 625 facings deposited in different runs [10]

<table>
<thead>
<tr>
<th>Run</th>
<th>Oxide content % (Intermediate contrast)</th>
<th>Hardness (knop)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31 ± 5</td>
<td>390 ± 30</td>
</tr>
<tr>
<td>2</td>
<td>16 ± 3</td>
<td>230 ± 15</td>
</tr>
<tr>
<td>3</td>
<td>16 ± 3</td>
<td>230 ± 15</td>
</tr>
<tr>
<td>4</td>
<td>15 ± 3</td>
<td>260 ± 20</td>
</tr>
<tr>
<td>5</td>
<td>12 ± 3</td>
<td>190 ± 15</td>
</tr>
<tr>
<td>6</td>
<td>18 ± 3</td>
<td>340 ± 20</td>
</tr>
<tr>
<td>7</td>
<td>25 ± 4</td>
<td>370 ± 30</td>
</tr>
<tr>
<td>8</td>
<td>14 ± 3</td>
<td>210 ± 15</td>
</tr>
<tr>
<td>9</td>
<td>14 ± 3</td>
<td>270 ± 20</td>
</tr>
<tr>
<td>10</td>
<td>11 ± 2</td>
<td>220 ± 15</td>
</tr>
<tr>
<td>11</td>
<td>16 ± 3</td>
<td>230 ± 20</td>
</tr>
<tr>
<td>12</td>
<td>16 ± 3</td>
<td>230 ± 20</td>
</tr>
<tr>
<td>13</td>
<td>18 ± 3</td>
<td>250 ± 20</td>
</tr>
<tr>
<td>14</td>
<td>24 ± 4</td>
<td>280 ± 30</td>
</tr>
<tr>
<td>15</td>
<td>17 ± 2</td>
<td>240 ± 15</td>
</tr>
<tr>
<td>16</td>
<td>12 ± 1</td>
<td>310 ± 20</td>
</tr>
<tr>
<td>17</td>
<td>18 ± 4</td>
<td>360 ± 30</td>
</tr>
</tbody>
</table>

Spraying distance and voltage both have a significant effect on the coating oxide content. Higher operating voltage leads to higher droplet temperature and smaller droplet size that both lead to reacting with more oxygen on the way for the molten droplets and finally higher oxide content in the coating microstructure. The influences of spraying parameters are discussed in followings;

**Influence of process parameters [10]**

The factors with the smallest P-value in the ANOVA analysis have the largest coefficients in the model, and so are predicted to have the largest effect on the outcome. Arc voltage and polyester powder injection rate are significant at a confidence level of greater than 999.99%, while spraying distance has a significant effect relative to random variation at a confidence level of 93.9%.

**a) Effect of arc voltage [10]:**

It has been shown that the stability of arc and the uniformity of droplet size are highly dependent on the arc voltage in twin wire arc spraying [17]. Lower voltages form low-temperature droplets that may be only partially molten when they reach the substrate surface. This impedes splat
formation and leads to the formation of pores between the coating splats. Higher voltages result in extra heating of the droplets that finally leads to significant shrinkage during solidification and shrinkage-pores formation [18]. Therefore, both higher and lower arc voltages than the optimum voltage increase the coating porosity content. That can be clearly seen in the perturbation graph presented in Figure 4-15 [10]. The maximum porosity content was observed for the voltage of 28 (v). Response surface plots, presenting the effect of arc voltage on coating porosity content, are shown in Figure 4-16 and Figure 4-17, respectively. The effect of arc voltage is not as big as polyester powder injection rate, but bigger than stand-off distance [10].

![Perturbation Graph](image)

*Figure 4-15 the perturbation plot of the response for input parameters by considering the middle level of the variables as the reference point [10]*
b) Effect of external polyester powder feeding rate [10]:

Based on ANOVA analysis presented in Table 4-7 and perturbation graph that is shown in Figure 4-15, the most significant factor affecting the coating porosity content is the external polyester powder feeding rate. It can be seen in Figure 4-15 that by keeping the voltage and distance in their middle levels, changing the external polyester powder feeding rate can change the coating porosity content by approximately 13 percent. The significance of this parameter can also be seen in response surface plots presented in Figure 4-16 and Figure 4-18. These results confirm the capability of high-porosity coating production by arc spray process using the suggested modification and optimized parameters. The effects of other parameters such as spraying distance and arc voltage on the coating porosity content are small compared to the effect of polyester powder content in the coating. By controlling the flow rate of polyester powder injection, the amount of intentionally added porosity to the arc sprayed coating can be controlled. The higher polyester powder feeding rate, the greater coating total porosity percentage [10].
c) Effect of stand-off distance [10]:

Few studies have addressed the effect of arc stand-off distance on coating porosity. Madaeini et al. showed that increasing the stand-off distance increases the porosity content of the coating [19], while other researchers claim that a shorter stand-off distance forms higher porosity content in the coatings [20], [21]. It also has been shown that shorter spraying distance provides better spreading and cohesion of the splats [22]. Large enough stand-off distance provides adequate length for acceleration of the molten droplets. However, too large a distance will allow the in-flight molten droplets to be cooled before impact. Mushy droplets cannot fill the voids in between the already deposited splats completely. In the present study, the effect of spraying distance on the coating porosity content was not significant, compare to arc voltage and polyester powder injection rate. This was confirmed by $P$-value of larger than 0.05 in ANOVA analysis results presented in Table 4-7. As shown in the perturbation plot in Figure 4-15, no significant change occurs in coating porosity content by changing the spraying distance from 100 mm to 200 mm. The reason is that
the spraying distance was selected in a short range close to optimum distance for good physical and mechanical properties specified by the past experiments [23]–[25]. However, there is a small increase in the porosity content by increasing the spraying distance. That can be seen in the surface plots of the response in Figure 4-16 and Figure 4-18 [10].

The developed model was employed to select arc spray process parameters for production of a coating with at least 20 percent porosity content that is permeable to gas fluids (hereafter “porous coating”), and a non-permeable low porosity alloy 625 facings (hereafter “dense coating”). About 100 solutions were suggested for each target by design expert software that the best ones with maximum desirability were selected for fabrication of dense and porous facings of sandwich panels. The suggested parameters which were employed for fabrication of dense and porous coating are presented in Table 4-9. Deposits were tested again for investigation of microstructural properties. It is observed that the resulted porosity contents are nicely matched with the predictions made by the model.

<table>
<thead>
<tr>
<th>Factors</th>
<th>unit</th>
<th>Levels</th>
<th>Dense* coating</th>
<th>Porous* coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc Voltage</td>
<td>V</td>
<td>32</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>Spraying Distance</td>
<td>cm</td>
<td>10</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Wire Feed Rate</td>
<td>m/min</td>
<td>7</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Gun Air Flow Rate</td>
<td>SCFM</td>
<td>60</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Gun Spraying Angle</td>
<td>Deg.</td>
<td>90</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>Gun Translation Speed</td>
<td>m/min</td>
<td>30</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Gun Raster Pattern</td>
<td>Pattern - steps(cm)</td>
<td>Linear - 4 Linear - 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore agent feeder disk rotation rate (RPM)</td>
<td>Revolutions per minute</td>
<td>0</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Pore agent feeder carrier gas flow rate (LPM)</td>
<td>liter per minute</td>
<td>0</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Produced facing’s porosity content</td>
<td>%</td>
<td>3 ± 1</td>
<td>24 ± 5</td>
<td></td>
</tr>
</tbody>
</table>

* “Dense” and “porous” expressions are used to address very low porosity coating and high-porosity gas permeable coating in this thesis
4.3.2 The effect of heat treatment [24]

It is commonly believed that annealing of thermally sprayed coatings leads to a better connection between the individual splats in the coating and ultimately to better mechanical properties for the skin [24], [26]. Diffusion bonding across the splats may occur during the annealing process at high enough temperatures. This phenomenon leads to the formation of metallurgical bonds between the splats and improves the overall cohesive strength of the skin. Godoy et al. showed that the residual stresses stored in thermal spray coatings can be released by annealing, which eventually improves the mechanical properties of these coatings [24], [27]. The presence of pores in the microstructure of the coating is also a significant factor in determining coating mechanical strength. Pores can act as stress concentrators that make crack formation and propagation easier inside the coating. It has been observed by Azarmi et al. that annealing can eliminate fine pores inside the coating microstructure and improves the mechanical properties [24], [28]. In addition to these findings, it was observed from the SEM images that the oxide content of the coating could be reduced by annealing the thermally sprayed coating in a vacuum furnace at high temperatures.

The mechanical performance of the thermally sprayed metallic foam core sandwich structures is an important factor for engineering applications. Thermal spray coating deposited on the foam substrate is considered as a structural element. The application of post-spraying heat treatment can improve the mechanical behavior of the sandwich structures by increasing the coating ductility and adhesion strength. This could result in reducing the danger of premature brittle failure in the skin [24], [28], [29].

The microstructures of the dense alloy 625 coatings deposited on 40 ppi nickel foam and then annealed at 900 °C for 1, 3 and 5 hours are shown in Figure 4-19 a to c respectively. Also Figure 4-20 a to c show the microstructure of the same alloy 625 coating annealed at 1100 °C for 1, 3 and 5 hours respectively [24]. From the SEM micrographs, higher annealing time and temperature lead to a more uniform microstructure and less oxide content. The most important role of heat treatment process can be expressed as breaking the network of oxide phase by diffusion of the neighbor splats through thin oxide layers. That can significantly improve the mechanical properties of the arc sprayed facings. Also, increasing the annealing time and temperature can result in a small decrease in the porosity content of the coating by eliminating tiny pores [28]. This effect was negligible for the samples annealed at 900 °C, and small for the samples annealed at 1100 °C. The
porosity and oxide content calculated from SEM images by image J software for the samples annealed under different conditions are presented in Table 4-10 [24].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity content (Vol. %)</th>
<th>Oxide content (Vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Sprayed</td>
<td>4 ± 1</td>
<td>25 ± 4</td>
</tr>
<tr>
<td>900-1</td>
<td>4 ± 1</td>
<td>21 ± 4</td>
</tr>
<tr>
<td>900-3</td>
<td>4 ± 1</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>900-5</td>
<td>4 ± 1</td>
<td>16 ± 3</td>
</tr>
<tr>
<td>1100-1</td>
<td>4 ± 1</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>1100-3</td>
<td>3 ± 1</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>1100-5</td>
<td>3 ± 1</td>
<td>12 ± 2</td>
</tr>
</tbody>
</table>
Figure 4-19 Microstructure of the alloy 625 arc sprayed coating after a) 1-hour annealing, b) 3 hours annealing, c) 5 hour annealing at 900 °C [24]

Figure 4-20 Microstructure of the alloy 625 arc sprayed coating after a) 1 hour annealing, b) 3 hours annealing, c) 5 hour annealing at 1100 °C [24]
The XRD patterns for heat-treated coatings are presented in Figure 4-21. The intensity of metallic phase Ni peaks for 5 hours annealed coating is close to the ones for alloy 625 wire presented in Figure 4-21, while as-sprayed coating shows strong oxide peaks. These results suggest that the higher annealing time and temperature can help with microstructural improvements in arc sprayed alloy 625 facings. A tensile test was performed on as-sprayed and annealed samples to investigate the effect of heat treatment on the mechanical behavior of facings. The results will be presented in chapter 5.

![XRD Pattern](image)

Figure 4-21 The XRD pattern for alloy 625 as feedstock, as-sprayed and annealed coatings
Gas permeability of the alloy 625 deposits

Figure 4-22 shows the schematic illustration of the gas permeability test apparatus designed by Professor Chandra’s research group and fabricated by Mechanical Engineering Department machine shop at University of Toronto. Disk shape samples of 120 mm in diameter were cut from the foam sheets coated by different sets of twin wire arc process parameters on only one face. Samples were mounted in the testing chamber cap and sealed using room temperature curable paste to ensure there in no gas leakage from the edges. Cap was placed over the chamber and sealed by a gasket. Compressed air was applied to the back of the samples after passing the pressure gauge, pressure regulator, and mass flow meter. The gas permission of the coatings was calculated based on the escaping mass of the air through the coating (shown on mass flow meter), pressure difference and surface area.

\[ k = \frac{Q \mu t}{A \Delta P} \]

Equation 4-2

Where \( Q \) is the air mass flow rate (m\(^3\)/s) through a cross-sectional area \( A \) (m\(^2\)), \( \mu \) is the air dynamic viscosity (Pa.s), \( \Delta P \) is the pressure drop (Pa) across the coating thickness \( t \) (m), and \( k \) is the permeability of the coating (m\(^2\)) [30].
The actual permeability test sample before mounting in the test setup, after mounting, and during the test is shown in Figure 4-23.

Figure 4-23 permeability test sample a) before mounting in the test apparatus b) after mounting in test apparatus c) during the permeability test d) during the permeability test with water on top to illustrate escape of gas

Three samples were tested for each of the dense and porous coatings. The average permeability of the coatings calculated using Darcy equation (Equation 4-2) was zero for the dense coating and $5.7 \times 10^{-14} \pm 1 \times 10^{-14}$ for the porous coating that confirms formation of open pores in the porous coatings, and consequently activating the film cooling effect on the thermally sprayed alloy 625 deposits.
References


[28] F. Azarmi, T. Coyle, and J. Mostaghimi, “Young’s modulus measurement and study of the


Chapter 5
Mechanical Behaviour

5.1 Introduction

Most of the sandwich structure applications are subject to bending loads. Although not all the high-temperature metallic foam core sandwich structures are subject to significant mechanical loads, the flexural stiffness of the sandwich panels is often important and indicates the level of integrity of these structures.

In this study, the mechanical behaviour of metallic foam core sandwich structures is investigated using several methods. First, each constituent’s mechanical properties are studied analytically and experimentally. The elastic modulus of the foam core is investigated using available theoretical models, followed by the presentation of the foam core compression test results. The yield strength and elastic modulus of alloy 625 facings produced by different sets of arc spray process parameters, and various heat treatment procedures, are investigated by tensile testing of freestanding facings, and compared with the available models. Finally, the overall mechanical performance of the arc sprayed sandwich panels are studied under four-point bending, and their measured flexural rigidity compared to analytical and FEM models.

Failure mode maps were generated from the available failure load equations using the experimentally measured parameters for the core and faces to predict the dominant initial failure mechanism for the sandwich panels. The results of visual inspection of sandwich panels during the four-point bending test were included in the generated maps to verify the predictions.

5.2 Mechanical behaviour of foam

5.2.1 Analytical model

As discussed in chapter 2, the elastic modulus of the foam is calculated from the slope of the compressive apparent stress-stain curve in its linear region. The elastic modulus of the foam can be modeled through a dimensional analysis of strut bending deflection. A micromechanical model has been developed by Gibson and Ashby [1], assuming that the mechanical properties of the foam
are mainly affected by the foam relative density. They considered strut bending as the dominant deformation mechanism and developed a model to relate the mechanical properties of the foam to its relative density. Gibson suggests that foam’s elastic modulus and yield strength are influenced by the ratio of foam density to solid material density or the solids’ volume fraction [2]. The elastic modulus of foam structures depends on the foam architecture and cannot be considered a material constant. The elastic modulus of an open pore metallic foam, \( E^* \), can be calculated using the equation below [2],[3];

\[
\frac{E^*}{E_s} = C_1 \left( \frac{\rho^*}{\rho_s} \right)^2
\]

Equation 5-1

Where, \( E^* \) is the elastic modulus of the foam, \( E_s \) is the elastic modulus of the solid material, \( C_1 \) is a constant equal to 0.98 for metallic foams [1], \( \rho^* \) is the foam density, and \( \rho_s \) is the solid material theoretical density. The properties of the foam materials used in the calculations are listed in Table 5-1. The density of nickel foam samples was calculated by dividing the average weight of cube shaped samples by their volume.

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic modulus of the bulk material (GPa)</th>
<th>Density of the bulk material (g/cm(^3))</th>
<th>Measured density of the foam (g/cm(^3))</th>
<th>Yield Strength of bulk material (MPa)</th>
</tr>
</thead>
</table>

Using the data presented in Table 5-1, the elastic modulus of the as-received nickel foam and Ni-Cr foam can be calculated as below:

\[
E^{*}Ni \hspace{1em} foam = 199 \times 0.98 \times \left( \frac{0.510}{8.9} \right)^2 = 0.64 \text{ Gpa}
\]

\[
E^{*}Ni - Cr \hspace{1em} foam = 214 \times 0.98 \times \left( \frac{0.550}{8.41} \right)^2 = 0.89 \text{ Gpa}
\]
Gibson and Ashby calculated the 0.2% offset yield strength of the foam using a similar model;

\[
\sigma_{0.2\%} = \alpha_1 \left( \frac{\rho^*}{\rho_s} \right)^{\frac{3}{2}} \sigma_{0.2\%}
\]

Equation 5-2

Where \(\sigma_{0.2\%}^*\) is the foam yield strength, \(\alpha_1\) is a dimensionless geometrical parameter \((\approx 1.5\) for nickel foam [8]), and \(\sigma_{0.2\%}\) is the yield strength of bulk material (Table 5.1). The yield strength of the nickel and Ni-Cr foams can be calculated using Equation 5-2 as below:

\[
\sigma_{0.2\%}^* \text{ Nickel foam} = 1.5 \times \frac{1}{2} \times \left( \frac{0.510}{8.9} \right)^{\frac{3}{2}} \times 60 = 0.617 \text{ MPa}
\]

\[
\sigma_{0.2\%}^* \text{ Ni-Cr foam} = 1.5 \times \frac{1}{2} \times \left( \frac{0.550}{8.41} \right)^{\frac{3}{2}} \times 110 = 1.3 \text{ MPa}
\]

It was assumed that the alloyed foam has a uniform distribution of Cr throughout the foam structure, and thus the effect of homogenizing time, after the alloying process, has not been considered in analytical studies of the foam mechanical properties.

### 5.2.2 Compression test results

Compression test results for as-received nickel foam and Ni-Cr foam samples (as chromized, after 2 hours annealing, and after 5 hours annealing) are presented in Figure 5-1. The apparent stress was calculated by dividing the applied load by the initial specimen cross-sectional area. It can be seen that all the foam samples showed a behaviour typical of ductile metallic foam structures [9]; a linear elastic region at low stresses, yield at a relatively higher stress, followed by a long plastic region with decreasing stress, and finally the densification region with increasing stress due to interaction of collapsed strut walls. It is clearly seen that the Ni-Cr foam has a higher yield strength than pure nickel foam. Also, annealing of the chromized foam improves its mechanical properties (higher collapse stress and higher elastic modulus).
The elastic modulus and yield strength of the foam structures extracted from compression test results are presented in Table 5-2.

We assumed that the Ni-Cr foam annealed for 5 hours is equivalent to the Ni-20Cr foam considered in analytical predictions using the Gibson and Ashby model. That is a fair assumption based on the EDS results presented earlier in Chapter 4. The yield strength obtained from the compression tests for each sample was comparable with the values calculated from the analytical model. Elastic modulus values obtained from the compression tests curves were significantly lower than the values calculated from the analytical model suggested by Gibson and Ashby [1]. It has been stated by Andrews et al. that when the compression test sample is small relative to cell size, the experimental values are significantly lower than analytically calculated ones [10]. Results show that both alloying and heat treatment substantially improve the mechanical properties of the foam.
### Table 5-2 compression test results

<table>
<thead>
<tr>
<th>Foam samples</th>
<th>Elastic Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received nickel foam</td>
<td>0.04 ± 0.01</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>As chromized Ni-Cr foam</td>
<td>0.05 ± 0.01</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>2 hour annealed Ni-Cr foam</td>
<td>0.07 ± 0.01</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>5 hours annealed Ni-Cr foam</td>
<td>0.10 ± 0.02</td>
<td>1.1 ± 0.2</td>
</tr>
</tbody>
</table>

Values are presented as: average of 3 measurements ± standard deviation

As the result of this section, 5 hours annealed Ni-Cr foam was chosen as the proper core for the high-temperature metallic foam core sandwich structures in this project. This type of foam offers almost the same oxidation resistance as the 2 hours annealed Ni-Cr, but exhibits considerably better mechanical properties than as-chromized and 2 hour annealed foams.

### 5.3 Mechanical behaviour of facings

#### 5.3.1 Analytical models

It is known that the elastic properties of isotropic, homogeneous, dense, multiphase materials are closely related to the amount of each phase present in the microstructure and their elastic moduli, and almost independent of microstructural features [11]. Thermal spray coatings show anisotropy in their structure in the directions parallel to spraying and parallel to the substrate surface due to the special shape of splats. The mechanical properties of anisotropic, non-homogeneous thermally sprayed coatings are highly affected by their microstructural features, such as pores, microcracks, splat boundaries, and undesired phases such as oxides in metal coatings. The microstructure and consequently mechanical properties of lamella type deposits produced by thermal spray methods are significantly different from those of dense bulk materials [3]. It is also very difficult to relate the thermal spray microstructure to the mechanical performance [12]. However, a few studies have presented empirical relationships between the microstructural characteristics and the mechanical properties of the thermally sprayed coatings [13], [14]. In general, only the effect of porosity content is considered as many assumptions have been made to develop idealized models. Some microstructural features such as oxide content, micro-cracks and splat boundaries are ignored in the models mentioned. Models describing the mechanical properties of thermal spray coatings are presented in the following. Dense and porous alloy 625 coatings will be evaluated using these models in Table 5-3.
Hashin-Hasselman model

This model is the most commonly used theoretical model for estimation of porous materials’ elastic modulus. It considers a linear relation between the inverse of the elastic modulus of the porous material (1/E*) and p/(1-p) where p is the volume fraction of all the splat interfaces, cracks, and pores (Equation 5-3) [15], [16].

\[
E^* = E_0 \left( 1 + \frac{Ap}{1-(A+1)p} \right)
\]

Equation 5-3

Where A is a constant (≈ -33.4 [17]) and E_0 is the dense material’s elastic modulus. E_0 for alloy 625 is 205 GPa [4]. The value of E* calculated for as sprayed dense and porous alloy 625 coatings are presented in Table 5-3.

Spriggs’ model

This empirical model is widely used for estimation of porous materials’ elastic modulus when the pores are distributed uniformly and have spherical shape [18];

\[
E^* = E_s e^{(-bp)}
\]

Equation 5-4

Where E_s is the elastic modulus of bulk alloy 625 (205 GPa), p is the volume fraction of the sum of pores, splat interfaces, and cracks; b is a constant (≈ 5.16 [17]). The estimated elastic modulus, using this model, for dense and porous coatings are presented in Table 5-3.

Zhao’s Model

It has been stated by many researchers that the thermally sprayed coatings show different mechanical properties when tested in directions parallel and perpendicular to the substrate surface plane [13], [19]–[21]. Zhao et al. [22] considered this anisotropy in the development of a model for plasma sprayed coatings that estimates properties both perpendicular (longitudinal) and parallel (transverse) to the substrate surface plane. In this model, an elliptical geometry is considered for the pores, with an aspect ratio (α, the equation below) of greater than one.

\[
\alpha = \frac{\text{radius in plane parallel to coating plane}}{\text{radius in plane perpendicular to coating plane}}
\]

Equation 5-5
The model is presented in two equations:

\[ E_T = \frac{E_m (1-p)}{1+2\pi \rho \alpha^{-2}} \] \quad \text{Equation 5-6}

\[ E_L = \frac{E_m (1-p)}{1+2\pi \rho} \] \quad \text{Equation 5-7}

Where \( E_T \) is the the elastic modulus in the direction parallel to the substrate surface plane, \( E_L \) is the elastic modulus in the direction perpendicular to the substrate surface, \( E_m \) is the dense material elastic modulus, \( \rho \) is the total volume fraction of porosity, and \( p \) is the volume fraction of elliptical pores. The elastic modulus of alloy 625 is 205 GPa and \( \alpha \) is 1.5 for our calculations. Based on observations, 30 percent of the pores in dense coatings, and 80 percent of pores in porous coatings are assumed to be elliptical. The estimated elastic modulus values for the alloy 625 coatings are presented in Table 5-3.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Porosity content (volume fraction)</th>
<th>Model used for calculation of estimated elastic modulus</th>
<th>Estimated Elastic modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As sprayed porous alloy 625</td>
<td>0.24</td>
<td>Hashin-Hasselman model</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spriggs’ model</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhao’s Model transverse</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhao’s Model longitudinal</td>
<td>63</td>
</tr>
<tr>
<td>As sprayed dense alloy 625</td>
<td>0.03</td>
<td>Hashin-Hasselman model</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spriggs’ model</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhao’s Model transverse</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zhao’s Model longitudinal</td>
<td>97</td>
</tr>
</tbody>
</table>

The elastic modulus values obtained from the Hashin-Hasselman model for 24% porous and 3% porous coatings are approximately 11% and 36% of the dense alloy 625, respectively. The values calculated by Spriggs’ model are greater than from the Hashin-Hasselman model. The values obtained from Zhao’s model sit between the other two models’ results.

128
5.3.2 Tensile strength tests

Stress-strain curves for the dense and porous alloy 625 facings, with different post-spray heat treatment conditions, are presented in Figure 5-2 and Figure 5-3 respectively. These data were used to extract elastic modulus, yield strength, and failure load and strain for each sample in the direction parallel to the facing planes. The ratio of stress to strain in the linear region of the curves specified the elastic modulus [3]. Each test was repeated five times for calculation of the facings’ mechanical properties. The calculated values for the sprayed facings, along with the mechanical properties of bulk alloy 625 material [4], are presented in Table 5-4. The stress-strain curve for as-sprayed alloy 625 tensile test samples consists of only a linear region that suggests negligible ductility for these coatings [3]. The elastic modulus for the as-sprayed samples with 3% and 24% porosity was about 30% and 20% of the bulk alloy 625, respectively.

Figure 5-2 stress-strain curve for alloy 625 facings – dense coating (3% porosity)
Table 5-4 mechanical properties of arc sprayed alloy 625 facings resulting from tensile test

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Post-spray treatment</th>
<th>Yield strength (MPa)</th>
<th>Strain at failure (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk alloy 625</td>
<td>N/A</td>
<td>320</td>
<td>15-20</td>
<td>205</td>
</tr>
<tr>
<td>Arc sprayed alloy 625 coating with 3% porosity (dense coating)</td>
<td>As sprayed</td>
<td>95 ± 15</td>
<td>0.7 ± 0.1</td>
<td>16 ± 5</td>
</tr>
<tr>
<td>1 hour at 1100 °C</td>
<td></td>
<td>162 ± 15</td>
<td>0.9 ± 0.1</td>
<td>21 ± 4</td>
</tr>
<tr>
<td>3 hours at 1100 °C</td>
<td></td>
<td>223 ± 10</td>
<td>1.1 ± 0.1</td>
<td>25 ± 4</td>
</tr>
<tr>
<td>5 hours at 1100 °C</td>
<td></td>
<td>293 ± 10</td>
<td>1.3 ± 0.2</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>Arc sprayed alloy 625 coating with 24 percent porosity (porous coating)</td>
<td>As sprayed</td>
<td>63 ± 15</td>
<td>0.5 ± 0.1</td>
<td>11 ± 5</td>
</tr>
<tr>
<td>1 hour at 1100 °C</td>
<td></td>
<td>123 ± 15</td>
<td>0.9 ± 0.1</td>
<td>15 ± 3</td>
</tr>
<tr>
<td>3 hours at 1100 °C</td>
<td></td>
<td>157 ± 20</td>
<td>0.9 ± 0.1</td>
<td>18 ± 5</td>
</tr>
<tr>
<td>5 hours at 1100 °C</td>
<td></td>
<td>220 ± 10</td>
<td>1 ± 0.1</td>
<td>24 ± 4</td>
</tr>
</tbody>
</table>

Values are presented as: average of 5 measurements ± standard deviation
As discussed before, even for dense arc sprayed coatings of alloy 625, the bonding between the coating’s splats is weak in as-sprayed coatings. That is mainly because the oxide phase formed on the surface of in-flight droplets may separate most of the splats during solidification. The lower elastic modulus observed for as-sprayed coating can be correlated to displacement of splats due to pores, cracks, and the oxide layer in the boundaries. Heat treatment, if done properly, can improve the splat-to-splat bonding and reduce the residual stresses stored in the microstructure of the coating during rapid solidification. The tensile test results confirm that heat treatment can significantly improve the elastic modulus, and yield strength of as-sprayed alloy 625 coatings. The yield strength and elastic modulus of the alloy 625 facings were improved by approximately 300% and 100%, respectively, after 5 hours annealing. The yield strength of the 5 hours annealed alloy 625 coating with 3% porosity is close to the bulk alloy 625. The ductility was also improved, but not as dramatically.

The values of elastic modulus extracted from the tensile test were lower than the ones estimated by the models discussed earlier. One of the facts that has not been considered in the models is the quality of bonding between the coating splats. While porosity can affect the mechanical properties considerably, weak connections between the splats or micro-cracks along the splat boundaries also play a critical role during tension testing. All in all, the models do not yield a good prediction of the elastic modulus of thermally sprayed coatings with a significant amount of intergranular oxides, such as the as-sprayed alloy 625.

None of the samples experienced a significant plastic strain before failure (examples in Figure 5-4). The failure of the facings is considered to be brittle at their yield point.
Heat treatment significantly affects the elastic modulus and yield strength of the foam core and faces. The flexural rigidity and failure of the sandwich structures will therefore also be affected. Changes in the mechanical behavior of the sandwich panels as a result of heat treatment will be studied in the next sections.

5.4 Mechanical performance of thermally sprayed sandwich structures

Metallic foam core sandwich structures made by thermal spray techniques can fail in different modes; face cracking, face yielding, core yielding and indentation. The dominant failure modes of conventional foam core sandwich structures under three-point bend testing has been analyzed and mapped by McCormack et al. [23], Bart-Smith et al. [24] and Triantafillou et al. [25]. Chen et al. [26] extracted the equations for each type of failure mode for sandwich structures tested by four-point bend testing.

The response of the sandwich structures under monotonic loading in four-pint bending has been investigated for beams with different geometries and annealed faces. Four-point bend testing allows different failure modes to be separated physically along the length of the sandwich samples;
indentation happens directly beneath the loading rollers, face yield occurs at the bottom face between the loading rollers, and core shear occurs between the loading and supporting rollers.

The load-displacement behaviour of the sandwich beams measured under four-point bending are compared with analytical and FEM results. Limit load formulae for elastic-ideally plastic beams were employed for analytical calculations. The initial failure load is taken as corresponding to peak load for each mode as well as the first deviation from linearity in the load-displacement curves. Based on the adhesion test data presented in Appendix G, it was assumed that the bonding between the foam core and the skins is perfect, and delamination does not occur in the case of thermally sprayed sandwich beams. Failure modes maps, with the architectural parameters of the sandwich beams as axes, are generated from the limit load equations [26], [27].

5.4.1 Prediction of the behaviour of sandwich panels under four-point bend loading

In the first section, analytical equations for flexural rigidity and failure strength of the sandwich panels under four-point bending are summarized. It is assumed that both thermally sprayed faces and metallic foam core are elastic-ideally plastic isotropic solids. Then, in the next section, a FEM method is employed to simulate the four-point bending test to obtain a more accurate prediction of the mechanical behavior of sandwich beams. The elastic-plastic curves of the core and faces obtained from the experiments are used in the FEM model.

5.4.1.1 Analytical analysis for flexural rigidity and failure strength

Consider a sandwich panel made of two identical faces of thickness t, a metallic foam core of thickness c, with a uniform width of b that is loaded by two cylindrical rollers of radius R and supported by the same type of rollers. Each loading roller carries half of the total applied load. The span between the supporting rollers is L, the span between the loading rollers is S, and the overhang distance beyond the supporting rollers is H (Figure 5-5).

The elastic deflection of the sandwich panel is affected by both shear and flexural deflections. Assuming the core is mostly under shear stress, the elastic deflection of the panel centre point can be approximately expressed by Equation 5-8.
\[
\Delta = \frac{F(L-S)^2(L+2S)}{48(EI)_{eq}} + \frac{F(L-S)}{4(AG)_{eq}}
\]

Equation 5-8

Where \(\Delta\) is the centre point deflection, \(F\) is the load, \((EI)_{eq}\) is the equivalent flexural rigidity, \((AG)_{eq}\) is the equivalent shear rigidity, and \(S\) and \(L\) are the loading and supporting spans, respectively [26], [28].

![Figure 5-5 Geometry of a sandwich structure in 4-point bending test](image)

Flexural rigidity of the sandwich panels is a key characteristic that indicates the integrity of the sandwich structure. Flexural rigidity, when the sandwich panel is subjected to 4-point bending, can be calculated based on the parallel axis theorem as below [25], [29], [30];

\[
(EI)_{eq} = \frac{Ef bt(d^*)^2}{2} + \frac{Ef bt^3}{6} + \frac{Ec bc^3}{12}
\]

Equation 5-9

Where \(EI_{(eq)}\) is the flexural rigidity, \(E_c\) and \(E_f\) are the elastic modulus of the core and facing materials, \(c\) is the core thickness, \(t\) is the facing thickness, \(d^*\) is the distance between the facings’ centre axes, and \(b\) is the sandwich panel width.

It is commonly believed that the core absorbs most of the shear stress in sandwich structures. The equivalent shear rigidity is [23], [26];
\[ (AG)_{eq} = \frac{G_c b (c+t)^2}{c} \approx G_c bc \]  \hspace{1cm} \text{Equation 5-10}

Where, \( G_c \) is the shear modulus of the core.

It is of particular importance to evaluate the failure strength of the sandwich structures in addition to their flexural rigidity. Upper bound calculations of different failure modes can be employed to obtain simple analytical equations. The facings and foam core are considered as ideally plastic, rigid solids of uniaxial strength of \( \sigma_{cy} \) and \( \sigma_{fy} \), respectively [26], [27]. The following summarized equations can be found in complete detail in the study by Ashby et al. [31].

**Face yield**

As discussed above, we exclude the brittle behavior of the facings from analytical analysis of the sandwich beams. That can be translated as we only study the annealed facings in this section. However, facing cracking that may happen for as-sprayed samples is investigated separately following this section.

For the thin face sandwich structures, face yielding occurs if the maximum in-plane tensile stresses in the facing exceed its yield strength (\( \sigma_{fy} \)), under a limit load \( F_{fy} \).

\[ F_{fy} = \sigma_{fy} \frac{4bt(c+t)}{L-S} + \frac{bc^2}{L-S} \sigma_{cy} \]  \hspace{1cm} \text{Equation 5-11}

**Core yielding**

Core yielding occurs if the maximum normal or shear stresses in the foam reach their yield strength. Shear forces are mainly carried by the foam core; this may result in plastic failure of the core. The point experiencing the maximum stress is at the interface of foam and skin. The critical value of the load for initiation of core yield at this point, has been derived by McCormack et al. [23]. They also presented expressions describing the stresses at the critical point for three-point bending:

\[
\sigma_{core} = \frac{PL}{4btc} \frac{E_c}{E_f} \hspace{1cm} \text{Equation 5-12}
\]

\[
\tau_{core} = \frac{p}{2bc} \hspace{1cm} \text{Equation 5-13}
\]
Therefore, the ratio of the shear to normal stress can be written as below;

$$\frac{\tau_{\text{core}}}{\sigma_{\text{core}}} = 2\frac{tE_f}{Le_c}$$  \hspace{1cm} \text{Equation 5-14}

For most of the cases the ratio of shear stress to normal stress in the foam core is large, and so the foam core can be assumed to be under pure shear stress as below [32]:

$$\tau = \frac{p}{2bc}$$  \hspace{1cm} \text{Equation 5-15}

Under flexural loading of the sandwich panels, two failure modes are possible for the foam core. In mode A, plastic hinges are formed at the loading points, directly beneath the loading rollers, and the shear stress is distributed throughout the foam core outside of the plastic hinges. In this mode failure of the core is by shear yielding, and overhangs extending to the right and left of the two support points are constrained to shear too [23], [33]. The failure load associated with this mode has been derived by Chen et al. [26] as;

$$F_{\text{CY-A}} = 2\frac{bt^2}{L-S}f_y + 2bc \tau_{cy} \left(1 + \frac{2H}{L-S}\right)$$  \hspace{1cm} \text{Equation 5-16}

Where; $\tau_{cy}$ is the shear yield strength of the metallic foam. Shear yield strength of the metallic foam is around two-thirds of the measured uniaxial strength in the compression test ($\tau_{cy} \approx \frac{2\sigma_{cy}}{3}$) [26], [31], [34]. From Equation 5-16 it can be understood that the core yield limit load increases with rising the overhang length, H.

In mode B, plastic hinges occur on both the loading points and the supporting points. In this mode, overhangs are unloaded and core failure occurs by core shear over length L between the support points. The failure load for mode B of the core yield has been derived by Chen et al. [26] as:

$$F_{\text{CY-B}} = 4\frac{bt^2}{L-S}f_y + 2bc \tau_{cy}$$  \hspace{1cm} \text{Equation 5-17}

Both equations presented for core yield failure are obtained from upper bound calculations of the actual failure load. Therefore, the lowest of these two failure loads is considered as the actual failure load. It has been confirmed that mode A of core yield happens for the sandwich beams with
small H while sandwich beams with large H have a lower value for \( F_{CY-B} \) compared to \( F_{CY-A} \). The overhang length at which transition from shearing mode A to mode B happens is [23], [33]:

\[
H_t = \frac{1}{2} \frac{t^2 \sigma_{yf}}{c \tau_{yc}}
\]

Equation 5-18

This also can be written as:

\[
\frac{C}{L} = \frac{\sigma_{yf} L}{\tau_{yc} 2H \left( \frac{t}{L} \right)^2}
\]

Equation 5-19

To illustrate the significance of H, let us take a set of architectural values of four-point bending test samples made by twin wire are spraying of alloy 625 followed by 3 hours annealing on 5 hours annealed Ni-Cr foam substrate. For a sandwich panel of c/L equal to 0.17, t/c equal to 0.05 and \( \frac{\sigma_{yf}}{\tau_{yc}} \) equal to 713, \( H_t \) is calculated to be 0.15 L. Therefore, an overhang length of 15% of supporting span (L) or more switches the core yield mechanism from mode A to mode B.

**Indentation**

Indentation of the sandwich panels occurs when the loading point crushes the foam, and the facing is bent to accommodate the foam core plastic deformation. The computation of the critical load for this failure mechanism is more complex than the mechanisms already discussed [23]. McCormack et al. [23] followed a finite element calculation, originally done by Miller [35] to develop an equation to approximate the critical load for indentation failure. Chen et al. [26] calculated this force for beams under four-point bend loading using upper bound calculations, and reported the expression below as the failure load for the indentation mode:

\[
F_I = 4bt \sqrt{\sigma_{fy} \sigma_{cy}}
\]

Equation 5-20

It has been reported that the lower bound calculations result in the same equation. Therefore, the exact value of the failure load can be found by this equation. However, all these calculations have been done based on beam theory, which is an approximation in our cases. The actual failure load may be different from what is found by this equation, as will be shown through experiment and FEM analysis [31].
**Face cracking**

Face cracking is when the facings are brittle, and fracture happens before yielding. This phenomenon is observed in most of the as-sprayed superalloys subject to bending loads. For this failure mode, the assumptions made for the previous methods, elastic-ideal plastic behavior, is not valid. Face cracking occurs if the maximum in-plane tensile stress in the facing exceeds its fracture strength \( \sigma_{ff} \). The simplified equation for fracture load is derived from the work done by Govaerts and Bhattacharjee [32] as:

\[
F_{fy} = \sigma_{ff} \frac{4bt (c+t)}{L-S} \quad \text{Equation 5-21}
\]

**Failure mode map for thermally sprayed metallic foam core beams**

We assume that the dominant failure mode of the sandwich structure is the one related to the lowest failure load. The failure mechanism of the sandwich panels can be shown in maps plotting a non-dimensional value of the upper bound failure load \( \bar{F} = \frac{F}{b_l \sigma_{fy}} \) on a graph with non-dimensional axes \( t/c \) and \( c/l \) for specific measures of \( \frac{\sigma_{yc}}{\sigma_{fy}} \). This approach has been employed by Gibson and Ashby [1] as well as Chen et al. [26].

The mechanical properties, like elastic modulus of the nickel and Ni-Cr foam and arc sprayed alloy 625, that are required for theoretical calculation of the flexural rigidity were obtained from the foam compression and facing tensile test results presented in Table 5-2 and Table 5-4, respectively.

Below, the transition line expressions found by setting each pair of failure mechanism loads equal are presented. These are used for generating the failure maps. Two different sets of loading and supporting span ratios were employed during the tests: one is \( L/S = 3 \) and the other \( L/S = 2 \). The equations are simplified for these two conditions as follows.

**Face yield – core yield mode B**

\[
\sigma_{fy} \frac{4bt (c+t)}{L-S} + \frac{bc^2}{l-s} \sigma_{cy} = 4 \frac{bt^2}{L-S} \sigma_{fy} + 2bc \tau_{cy} \quad \text{Equation 5-22}
\]

For \( L/S = 2 \):
\[
\left( \frac{c}{L} \right) = \frac{0.9 \sigma_{cy}}{4 \left( \frac{t}{c} \right)^2 \sigma_{fy}} 
\]
Equation 5-23

For L/S=3:

\[
\left( \frac{c}{L} \right) = \frac{0.67 \sigma_{cy}}{4 \left( \frac{t}{c} \right)^2 \sigma_{fy}} 
\]
Equation 5-24

Face yield – indentation

\[
\sigma_{fy} \frac{4bt}{L-S} \left( \frac{c}{t} \right)^2 + \frac{bc^2}{L-S} \sigma_{cy} = 4bt \sqrt{\sigma_{fy} \sigma_{cy}} 
\]
Equation 5-25

For L/S= 2:

\[
\left( \frac{c}{L} \right) = \frac{\frac{2}{\sigma_{fy}} \sqrt{\sigma_{fy} \sigma_{cy}}}{\left( 4 + 4 \left( \frac{t}{c} \right)^2 + \frac{1}{\left( \frac{t}{c} \right)} \frac{\sigma_{cy}}{\sigma_{fy}} \right)} 
\]
Equation 5-26

For L/S=3:

\[
\left( \frac{c}{L} \right) = \frac{\frac{2.68}{\sigma_{fy}} \sqrt{\sigma_{fy} \sigma_{cy}}}{\left( 4 + 4 \left( \frac{t}{c} \right)^2 + \frac{1}{\left( \frac{t}{c} \right)} \frac{\sigma_{cy}}{\sigma_{fy}} \right)} 
\]
Equation 5-27

Indentation – core yield mode B

\[
4bt \sqrt{\sigma_{fy} \sigma_{cy}} = 4 \frac{bt^2}{L-S} \sigma_{fy} + 2bc \tau_{cy} 
\]
Equation 5-28

For L/S= 2:

\[
\left( \frac{c}{L} \right) = \frac{\frac{\sigma_{fy} \sigma_{cy}}{\sigma_{fy} + \frac{1}{\left( \frac{t}{c} \right)} \frac{\sigma_{cy}}{\sigma_{fy}}}}{2 \left( \frac{t}{c} \right)} 
\]
Equation 5-29

For L/S=3:
\[
\left( \frac{c}{L} \right) = \sqrt{\frac{\sigma_{fy}\sigma_{cy}}{\frac{1}{3}\left(\frac{\sigma_{cy}}{\sigma_{fy}}\right)}} \frac{1.5\left(\frac{c}{L}\right)}{\left(\frac{c}{L}\right)^2}
\]

Equation 5-30

Core yield mode A – Core yield mode B

\[
\frac{c}{L} = \frac{\sigma_{fy} L}{\sigma_{yc} 2H} \left(\frac{t}{L}\right)^2
\]

Equation 5-31

The experimentally measured values of the yield strength for the samples made of Ni foam and annealed Ni-Cr foam as the core (Table 5-2) and annealed alloy 625 deposits with 3% and 24% porosity as the facings (Table 5-4) were used to plot the failure maps for the sandwich structures. Only annealed facings were considered in plotting the failure mechanism maps, as the brittle behavior of the as-sprayed coatings is not recommended for the target applications and does not satisfy the assumptions made for generating the failure load equations. Furthermore, the brittle fracture of the skin is not an option in the sandwich structure design. It is also assumed that the overhang length (H) is long enough that the core fails only in mode B. The generated failure maps are shown in Figure 5-6 to Figure 5-13. These are sample plots, which can be extended to a wider range of sandwich architectures and materials. The assumptions used to plot each map are stated above the plots.

It can be clearly in the maps that the dominant failure mode for thin faces (small t/c) and long beams (small c/L) is face yielding. Also, the face failure region becomes wider in both axes by increasing the face porosity content and by increasing the yield strength of the core.

From the maps, it is observed that the boundary between indentation and core yield failure modes has a large curvature, with the core yield mode dominating at intermediate values of t/c. That is due to the formation of plastic hinges during core yielding. The core yield failure load increases quadratically by increasing the skin thickness (t/c ratio in the map) because of the contribution of the faces in bending, see Equation 5-16 and Equation 5-17 [26]. The maps plotted for selected architectures illustrate that the dominant failure mode for thermally sprayed sandwich beams in this study is core yielding. The considerable difference between the mechanical strength of the faces and the core justifies these results.
Once again, in the current study, only plastic failures have been investigated based on the assumptions we made about using annealed faces for the sandwich structures. Sudden brittle fracture of the skin was observed in the four-point bending test performed on as sprayed sandwich panels (with no annealing post-treatment). This brittle elastic behaviour of the faces and their consequent catastrophic failure is not acceptable in most of the sandwich structure applications, so we only considered annealed sandwich panels for further investigations of the failure mode.
Figure 5-6 Failure mode map for sandwich structures made of pure nickel foam and 24\% porosity coating with the ratio of L/S=2

Figure 5-7 Failure mode map for sandwich structures made of pure nickel foam and 24\% porosity coating with the ratio of L/S=3

Figure 5-8 Failure mode map for sandwich structures made of pure nickel foam and 3\% porosity coating with the ratio of L/S=2

Figure 5-9 Failure mode map for sandwich structures made of pure nickel foam and 3\% porosity coating with the ratio of L/S=3
Figure 5-10 Failure mode map for sandwich structures made of Ni-Cr foam and 24% porosity coating with the ratio of L/S=2

Figure 5-11 Failure mode map for sandwich structures made of Ni-Cr foam and 24% porosity coating with the ratio of L/S=3

Figure 5-12 Failure mode map for sandwich structures made of Ni-Cr foam and 3% porosity coating with the ratio of L/S=2

Figure 5-13 Failure mode map for sandwich structures made of Ni-Cr foam and 3% porosity coating with the ratio of L/S=3
5.4.1.2 FEM modeling

In order to accurately predict the load versus displacement behavior of the metallic foam core sandwich structures, finite element analysis (FEM) using ANSYS workbench V. 15 was employed for selected architectures of the thermally sprayed sandwich beams. Sandwich materials are challenging to model due to the different orthotropic properties of the constituents, therefore selection of the proper element types, the configuration of layers and connections and finally boundary conditions have to be done carefully. The properties of each layer have to be defined separately, using the experimental data gathered from the mechanical tests.

FEM analysis was conducted using the static structural module employing tetrahedron elements for meshing. The range in the number of elements which resulted in a constant response to the bending load was determined by varying the number of elements; 69168 elements and 74838 nodes were used in the calculations reported here. The facings and the core were considered to be bonded. The supporting rollers were fixed supports and the boundary conditions for the loading rollers were directional displacements in the negative direction of the Y-axis while no displacement was allowed in other directions. The material properties required for simulations were obtained from the mechanical test results on the foam and facings. The stress-strain behaviour for the foams and facings were represented using experimentally obtained curves for the sample whose yield strength was closest to the average yield strength.

FEM was performed for both linear and nonlinear responses, allowing for large deflections. The load-displacement graphs were plotted using the data generated by ANSYS. A typical solution by ANSYS is shown in Figure 5-14.
Figure 5-14 Typical sandwich beam modeled in ANSYS workbench V. 15. This image captures distribution of elastic strain in the core in the linear region.

The load-deflection curves were plotted for modeled architectures using the values tabulated in the solution results; force reaction and directional deformation in -Y direction.

Following this section, comparisons between the experimental results, the analytical studies, and FEM models will assist us in better understanding and predict the behaviour of arc sprayed metallic foam core sandwich panels. The sandwich structure failure mode maps are presented and discussed as the main outcome of this portion of the work.

5.4.2 Four-point bending tests

Four point bending has been commonly employed as an appropriate technique for characterizing the rigidity of sandwich beams [36]–[39]. The flexural rigidity of the metallic foam core sandwich structures was determined from the elastic region of the load-displacement curves resulting from 4-point bending tests. The rigidity (EI<sub>eq</sub>) can be calculated from the expression suggested by Allen [29], which relates the center point deflection (\(\Delta\)) to the applied load (\(P\)) and flexural rigidity (EI<sub>eq</sub>):

\[
\Delta = \frac{P(L-S)^2(L+2S)}{48EI_{(eq)}} + \frac{P(L-S)}{4U}
\]

Equation 5-32
Where \( U \) is the shear rigidity, \( S \) is the loading span, \( L \) is the support span, and \( P \) is the applied load. Center-point deflection on a typical arc sprayed sandwich structure is shown in Figure 5-15. \( \Delta \) can be approximated as the universal testing machine crosshead movement.

![Figure 5-15 Centre point deflection for a typical thermally sprayed sandwich beam after 4-point bending load](image)

Figure 5-16 presents a typical load-displacement curve obtained from a 4-point bending test of a metallic foam core sandwich panel with 3 hours-annealed dense arc sprayed alloy 625 facings of 1 mm.

![Figure 5-16 four-point bending load-stroke curves for a 3 hours-annealed dense arc sprayed alloy 625 coating of 1 mm thick](image)

Curves consist of several stages; the initial linear stage reflects the elastic behaviour of the beam. It is followed by a stage exhibiting a non-linear increase in load due to plastic deformation, and finally, a rapid decrease happens in the load as a result of cracking and fracture. The plastic deformation stage is not seen for the as-sprayed specimens due to brittle failure of the facings before any plastic deformation.
The flexural stiffness of the sandwich panels, $EI_{eq}$, were determined both theoretically using Equation 5-9, and experimentally from the 4-point bending force-displacement graphs in their elastic region, using Equation 5-32 (Table 5-5). Sandwich structure specimens employed for 4-point bending experiments were fabricated with different geometries, facing thicknesses, and porosity content. The heat treatments for fabricated sandwich panels were conducted at 1100°C following the promising behaviour of the heat treated facings presented in section 5.3.2.

From the results presented in Table 5-5, it can be seen that heat treatment of sandwich panels for 3 hours at 1100 °C improved their mechanical behaviour (flexural rigidity). Also, in comparison with the theoretical results, the experimentally obtained flexural rigidity values were lower. In addition to determining the flexural rigidity of the fabricated sandwich panels, four-point bending tests were used to determine what failure mechanism acts first for different types of sandwich panels. These tests were run by increasing the load in a stepwise manner, unloading after each step to inspect the surface and core of the sandwich beam for any signs of failure, then reloading. A typical load-displacement graph resulting from this type of bending test is presented in Figure 5-17.
Table 5-5 flexural rigidity of thermally sprayed metallic foam core sandwich beams prepared with various conditions

<table>
<thead>
<tr>
<th>sample</th>
<th>Foam thickness (mm)</th>
<th>Supporting span, L (mm)</th>
<th>Facing Thickness (µm)</th>
<th>Facing Porosity (%)</th>
<th>Post Treatment (Temperature ºC - Time Hours)</th>
<th>( EL_{(eq)} ) Theoretically calculated rigidity, Nm²</th>
<th>( EL_{(eq)} ) Experimentally measured rigidity, Nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>3%</td>
<td>As sprayed</td>
<td>2.04</td>
<td>6 ± 0.5</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>60</td>
<td>500</td>
<td>3%</td>
<td>As sprayed</td>
<td>11.025</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>60</td>
<td>1000</td>
<td>3%</td>
<td>As sprayed</td>
<td>24.2</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>3.2</td>
<td>7 ± .05</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>60</td>
<td>500</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>17.22</td>
<td>16.5 ± 1</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>60</td>
<td>1000</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>37.81</td>
<td>27 ± 3</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>24%</td>
<td>As sprayed</td>
<td>1.4</td>
<td>5 ± 0.4</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>60</td>
<td>500</td>
<td>24%</td>
<td>As sprayed</td>
<td>7.58</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>60</td>
<td>1000</td>
<td>24%</td>
<td>As sprayed</td>
<td>16.7</td>
<td>15.5 ± 0.5</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>2.3</td>
<td>6.5 ± 0.5</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>60</td>
<td>100</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>12.4</td>
<td>12 ± 1.5</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>60</td>
<td>1000</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>27.23</td>
<td>23 ± 2</td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td>60</td>
<td>100</td>
<td>3%</td>
<td>As sprayed</td>
<td>8</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>14</td>
<td>20</td>
<td>60</td>
<td>500</td>
<td>3%</td>
<td>As sprayed</td>
<td>42.03</td>
<td>31 ± 3</td>
</tr>
<tr>
<td>15</td>
<td>20</td>
<td>60</td>
<td>1000</td>
<td>3%</td>
<td>As sprayed</td>
<td>88.2</td>
<td>71 ± 4</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
<td>60</td>
<td>100</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>12.62</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
<td>60</td>
<td>500</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>65.7</td>
<td>48 ± 4</td>
</tr>
<tr>
<td>18</td>
<td>20</td>
<td>60</td>
<td>1000</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>137.81</td>
<td>105 ± 8</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>60</td>
<td>100</td>
<td>24%</td>
<td>As sprayed</td>
<td>5.56</td>
<td>8 ± 1.2</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>60</td>
<td>500</td>
<td>24%</td>
<td>As sprayed</td>
<td>28.9</td>
<td>24 ± 2</td>
</tr>
<tr>
<td>21</td>
<td>20</td>
<td>60</td>
<td>1000</td>
<td>24%</td>
<td>As sprayed</td>
<td>60.7</td>
<td>40 ± 2</td>
</tr>
<tr>
<td>22</td>
<td>20</td>
<td>60</td>
<td>100</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>9.1</td>
<td>10.5 ± 1</td>
</tr>
<tr>
<td>23</td>
<td>20</td>
<td>60</td>
<td>500</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>47.3</td>
<td>37 ± 4</td>
</tr>
<tr>
<td>24</td>
<td>20</td>
<td>60</td>
<td>1000</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>99.2</td>
<td>83 ± 5.5</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>100</td>
<td>100</td>
<td>3%</td>
<td>3 hours at 1100</td>
<td>12.62</td>
<td>12.5 ± 1.5</td>
</tr>
<tr>
<td>26</td>
<td>20</td>
<td>100</td>
<td>100</td>
<td>24%</td>
<td>3 hours at 1100</td>
<td>9.1</td>
<td>11 ± 1</td>
</tr>
</tbody>
</table>
The failure modes observed for the experimentally investigated samples (Table 5-5) are included in the failure maps presented in Figure 5-11 and Figure 5-13. In general, there is in an acceptable agreement between the experimentally determined failure modes and the ones predicted from the analytical calculations. However, there were two samples with geometrical specifications close to the indentation-core yield boundary (samples number 17 and 23) for which the experimental results did not agree with the analytical predictions for the failure mode. These samples failed by a combination of indentation and core yield although they are located in the indentation region of the maps.

The predicted and observed failure modes are compared in typical load-stroke curves of selected test specimens failing under core yielding, face failure (yielding or cracking), and face indentation in the following sections. The analytical model plots and the curves resulting from FEM modeling are embedded in these graphs for better evaluation of the accuracy of the predictions. FEM curves represent the behaviour expected for a sandwich consisting of a face and core each of which exhibits average behaviour.
**Core Yielding**

Figure 5-18 a shows the load versus displacement curves obtained from the analytical method, FEM and experiment for specimen number 5 in Table 5-5 with a face thickness of \( t = 0.5 \) mm and core thickness of \( c = 10 \) mm, loading span of \( s = 20 \) mm and supporting span of \( L = 60 \) mm and overhang length of \( H = 3 \) mm. This overhang length is shorter than the core yield modes transition value, and leads to core failure by mode A. In contrast, Figure 5-18 b presents a specimen with the same criteria but with longer overhang length, \( H = 15 \) mm, sufficient to fail by core yield mode B. For both samples it was visually confirmed that the failure was by core yield and plastic hinges formed on the faces. In both cases, the skin is not stiff enough to carry the applied loads, and the overall mechanical stiffness is dependent on the core strength. The load-displacement curves show a linear behavior in the beginning that is representative of the elastic region and then plastic deformation starts once the applied load causes a shear stress of more than the foam’s yield point. The non-linear region of the curve describes the plastic deformation of the foam core. The experimentally obtained load-displacement curve shows a peak with scattered microcracks occurred in the foam core during the bending test after the peak load. There can be seen 85% agreement between the experimentally measured failure load, and the FEM predictions for yield point. The analytically calculated failure load is a little larger than FEM and experimental values, which could be due to the assumptions made during analytical work (simple beam theory). It can also be observed that the predicted elastic stiffness by FEM and experiment are in close agreement (Table 5-5).
A series of experiments were performed to monitor the transition between mode A and mode B of the core yield failure mechanism of the sandwich beams. The beam dimensions used for these experiments were core thickness of $c = 10$ mm, facing thickness of $t = 0.5$ mm, loading span of $S = 20$ mm and supporting span of $L = 60$ mm, with overhang length changing in the range of $H = 2$ to $30$ mm. The peak loads predicted by the analytical calculations, FEM predictions and experimental...
measurements are presented in Figure 5-19. While there is a difference between the peak load obtained from three different methods, all of them show a transition from mode A to mode B at $H = 4 \text{ mm}$. That was confirmed by visual observation of the experimental specimens.

![Figure 5-19 peak loads associated with the core yield mechanism as a function of overhang length](image)

**Indentation**

The failure maps presented earlier in this chapter suggest that the metallic foam core sandwich beams fail under indentation mode when the core thickness is sufficiently large in relation to the loading span. Also, indentation becomes dominant when the coating thickness is larger than the values resulting in face yielding and smaller than values leading to core yield. This mechanism is very hard to identify compared to core and skin yielding mechanisms. The experimental curve obtained from a specimen with a core thickness of $c= 10 \text{ mm}$, facing thickness of $t= 0.1 \text{ mm}$, loading span of $L= 60 \text{ mm}$ and supporting span of $S= 20 \text{ mm}$ is presented along with FEM and analytical results in Figure 5-20. It can be seen that the analytically predicted failure load (peak load) is higher than both FEM and experimental results.
Equation 5-20 suggests that the indentation failure load has a linear relation with the facing thickness. The failure load of sandwich beams with a core thickness of $c=20$ mm, loading span of $L=60$ mm, facing thicknesses of $t=0.1$, 0.25 and 0.50, are plotted in Figure 5-21. There is acceptable agreement with the predictions and experimental observations that the peak load increases linearly with increasing the facing thickness. For the samples with $t = 0.5$ mm, a combination of core yielding and indentation was observed. That is understandable due to being close to the boundary of the core yield and indentation regimes on the related failure map.
Face Failure

As predicted in the failure mode maps, the dominant failure mode for small facing thicknesses and supporting spans large in relation to the core thickness is face yielding. A typical load versus displacement plot for the specimens failed under face yielding is shown in Figure 5-22. For a specimen with a core thickness of $c=20$ mm, facing thickness of $t=0.1$ mm, loading span of $L=100$ mm and supporting span of $S=20$ mm (specimen number 26 in Table 5-5). It can be seen that the load increases until the tension in the facing leads to a strain equal to the facing’s ductility. It can be observed that compared to analytical calculations, the FEM and experimental results are close in flexural stiffness (slope of the linear region) and failure load (yield point). However, there is still a considerable difference between these results. The reason for such disagreement could be the effect of foam strut tips embedded in the thermally sprayed facings that reduce the skin thickness in some spots and reduce the mechanical strength of the skin. That has a bigger effect on the mechanical properties evaluations when skin failure is the dominant failure mode.

Figure 5-21 peak loads associated with the indentation mechanism as a function of facings’ thickness
Equation 5-11 suggests that the skin failure load is linearly related to $(L-S)^{-1}$. A set of experiments were conducted by varying the $(L-S)$ value to verify this effect. The peak loads measured for these samples experimentally and determined by the analytical method and FEM are presented in Figure 5-23. The measured values confirm the inverse relation between the peak load and $(L-S)$ suggested by the analytical formula which is also confirmed by FEM results.

![Figure 5-22 Typical load-stroke curve resulted from sample failed by face yielding mechanism](image1)

![Figure 5-23 Peak loads associated with the face yield mechanism as a function of (L-S)](image2)
So far, all the studies were based on the assumption that facings are ductile as a result of annealing at 1100 °C for three hours. This assumption allowed us to perform the calculations considering the facing as an ideal plastic material. However, this assumption is not valid for the as-sprayed faces, where the deposit shows an elastic-brittle behavior. The failure mechanism for as sprayed sandwich beams was face cracking. The analytical methods could not be used for this failure mode, and therefore only the experimentally obtained curve is presented for a 0.5 mm thick as-sprayed coating on a sandwich beam of 10 mm thick and loading span of 60 mm in Figure 5-24. It can be seen that as soon a deviation from the linear path occurs in the load-displacement curve, the load drops, indicative of crack formation in the skin. The visually inspected samples confirmed such an initial failure mode.

![Face Cracking](image)

**Figure 5-24 Typical load-stroke curve resulted from sample failed by face cracking mechanism**

The flexural behavior of sandwich structures made with a pure nickel foam core or an annealed Ni-Cr foam core 0.5 mm thick with annealed alloy 625 faces is compared in Figure 5-25. It is clear that the foam mechanical strength plays a critical role in stiffness and yield strength of the beam.
The effect of porosity content and heat treatment of the metallic foam core sandwich structures with 500 µm facing thickness are shown for two different skin porosity contents; 3 % and 24 % in Figure 5-26 and Figure 5-27, respectively.

**Figure 5-25** Four-point bending load-stroke curve for 500 µm-thick alloy 625 facings sandwich structure with 10 mm-thick-core of pure nickel and Ni-Cr heat treated alloyed foam

The effect of porosity content and heat treatment of the metallic foam core sandwich structures with 500 µm facing thickness are shown for two different skin porosity contents; 3 % and 24 % in Figure 5-26 and Figure 5-27, respectively.

**Figure 5-26** the effect of annealing on the load-stroke curve for 500 µm thick facings with 24% porosity/20 mm thick core sandwich panels
It can be seen that use of Ni-Cr foam structures annealed for 5 hours at 1200 C can improve the mechanical properties of the sandwich beam. In chapter 4, we also saw that the oxidation resistant of this type of foam is considerably better that the pure nickel foam. Also, annealing of alloy 625 deposits for long enough time improves their mechanical properties. These findings were valid for sandwich structures made by both 3% and 24% porosity facings.

5.5 Summary of the results

Mechanical behaviour of the metallic foam core:

- The analytically calculated values of elastic modulus for pure nickel and Ni-Cr 5 hours annealed foams were 0.64 GPa and 0.89 GPa respectively.

- The experimentally measured value of elastic modulus for pure nickel and Ni-Cr 5 hours annealed foams were 0.04 GPa and 0.1 GPa respectively.

- The analytically calculated value of yield strength for pure nickel and Ni-Cr 5 hours annealed foams were 0.617 Mpa and 1.3 Mpa Respectively.
- The experimentally calculated value of yield strength for pure nickel and Ni-Cr 5 hours annealed foams were 0.5 MPa and 1.1 MPa respectively.

- Elastic modulus and yield strength of the as alloyed Ni-Cr foam was not significantly different with pure nickel foam. However, this difference increased by increasing the Ni-Cr foam annealing time to make uniformly alloyed struts.

- The use of 5 hours annealed Ni-20%Cr foam is suggested to increase the stiffness of all metal foam core sandwich structures for high-temperature applications.

**Mechanical behavior of the facings**

- Experimentally measured mechanical properties of the arc sprayed alloy 625 facings were significantly lower than the analytically predicted values. This is because thermal spray deposits are anisotropic by nature and contain significant amounts of micropores, oxide layers, and weak splat boundaries. Mechanical properties of the facings were improved by heat treatment but still far from the ones calculated by the available models.

- Increasing the porosity content of the skin lowers its mechanical properties. The experimentally obtained elastic modulus of the 3% porosity alloy 625 annealed for 3 hours was 25 GPa compared to 18 GPa for 24% porosity coating. The measured value of yield strength for the annealed facings was 223 MPa and 157 MPa for 3% and 24% porosity coatings respectively.

- The elastic modulus of the low porosity alloy 625 coating was found to be 7% of the conventional (bulk) alloy 625 for as sprayed deposits and 12% for 3-hours annealed deposits.

- The elastic modulus of the high porosity alloy 625 coating was found to be 5% of the conventional (bulk) alloy 625 for as sprayed deposits and 8% for 3-hours annealed deposits.

**Mechanical behaviour of the sandwich structure**

- The flexural rigidity and failure load of sandwich beams were predicted by analytical models, FEM, and measured by four-point bending tests.
- The value of the flexural rigidity obtained for different architectures by FEM and experiments were close, while there was a difference in the yield points. The analytically calculated failure load was significantly higher than the experimental measurements.

- The dominant failure mode for sandwich structures with intermediate face thickness and foam thickness was core yielding.

- The dominant failure mode for thin facing panels was face yielding.

- The failure modes that were predicted analytically and by FEM were very close to the actual observations, with a few exceptions for architectures close to the boundary between different failure regimes.
References


Chapter 6
Closure

6.1 Results and Conclusions

This thesis reports the development and characterization of open-cell metallic foam core sandwich structures suitable for high-temperature applications, fabricated by the arc spray process.

The microstructural and mechanical properties of pure nickel foam and Ni-20%Cr nickel foam were studied. The results of high-temperature oxidation tests and characterization of mechanical properties showed that Ni-20%Cr annealed for 5 hours at 1200 ºC, and alloy 625 annealed for 3 hours at 1100 ºC are the best candidates among those investigated for the production of high-temperature metallic foam core sandwich structures by the arc spray method.

The mechanical performance of the sandwich panels was studied through analytical methods, finite element modeling (FEM) and experimentally by four-point bending tests. The effects of the strength and thickness of the core; the thickness, heat treatment and porosity of the facings; and the span length were investigated.

The following conclusions are drawn from the results of this project:

- The pack cementation process can be used for alloying commercially available pure nickel foam to produce Ni-20% Cr foams with higher mechanical strength and improved high-temperature oxidation resistance.

- The porosity of arc sprayed coatings can be controlled by appropriate selection of the deposition process parameters. The relations between deposition parameters and porosity can be identified efficiently through the use of statistically designed experimental trials (DOE).

  ✓ The arc spray process is capable of producing low porosity (3%), low oxide content (13%) skins on the metallic foam substrate for fabrication of metallic foam core sandwich structures.
The arc spray process can be modified by adding a pore agent injector to produce highly porous coating with porosity content of above the normal ranges achievable by conventional arc spray systems. It was shown by permeability tests that 20% porosity is high enough to allow gaseous fluid to permeate through the cross section of arc sprayed deposits and produce a film cooling effect.

- The elastic modulus of the arc sprayed alloy 625 was determined by tensile testing and found to be affected by the porosity content. The elastic modulus of the as-sprayed alloy 635 with 3% and 24% porosity content was 7% and 5% of conventionally processed bulk alloy 625, respectively. This is due to weak bonding between the splats as well as the effect of pores inside the deposits.

- An annealing heat treatment at 1100°C improved the mechanical properties of the alloy 625 deposits for both 3% and 24% porosity content types. The elastic modulus of the 3% and 24% coatings improved by around 60% after 3 hours annealing at 1100°C.

- The elastic modulus of the foams measured experimentally was significantly below the predictions of the analytical model. That may be due to the small specimen size relative to the foam cell size.

- The flexural rigidity and failure load of sandwich panels fabricated from foam cores and faces with a range of mechanical properties and with a range of architectures were measured experimentally and compared with the predictions made by the analytical methods and finite element modeling. The FEM results were close to experimentally measured flexural rigidity; there was less agreement between the predicted and measured failure loads. The failure load calculated by analytical methods was significantly higher than the experimental results for the face yielding failure mode; that might be because the face becomes very thin on top of foam strut tips. Analytical results were closer to experimental findings for the core yield mode, although still considerably higher. There was better agreement among the three methods for the indentation failure mode.
• The flexural rigidity of the thermally sprayed sandwich panels was increased significantly by annealing of the skins at 1100 °C for 3 hours. Higher core thickness, less porosity in the skins, and thicker skins yield a higher flexural rigidity for the sandwich structures.

• Failure mode maps generated by analytical methods exhibited acceptable agreement between the predicted and observed failure modes. However, there was some disagreement for the specimens which fell close to the boundary line between different failure mode regions. A combination of two different failure modes was observed for such samples.

6.2 Major contributions

• Development of a cost-effective, flexible and rapid procedure for fabrication of high-temperature metallic foam core sandwich structures.

• Evaluation of the effect of alloying on the mechanical properties and oxidation resistance of commercially available nickel foam structures.

• Development of a modified arc spray process capable of depositing alloy 625 coatings with controllable porosity content.

• Measuring the mechanical properties of alloy 625 deposits by tensile test experiments and investigating the effect of porosity content and heat treatment on the microstructure and consequently mechanical behavior of the deposit.

• Evaluating the mechanical behavior of the thermally sprayed metallic foam core sandwich structures using analytical, FEM and experimental methods and comparing the results.

• Generating failure mode maps for metallic foam core sandwich structures made of nickel and Ni-Cr foam core and alloy 625 coatings, for different architectures, and comparing with experimental observations.
6.3 Recommendations for future work

- Extend the failure mode maps to a wider range of variables, such as foam density, coating materials and processing conditions and beam architecture.

- Model the foam structure by FEM as a porous media, instead of considering it a bulk material with reduced mechanical properties.
Appendix A: Drawing for pack chromizing retort used for alloying the pure Ni foam

A1. Drawing of the pack cementation retort

A2. Schematic of the pack cementation retort
Appendix B: Curing process and transformation of filling paste epoxy to high strength thermoset resin

Figure A3. Curing mechanism of Acrodur resin used in the preparation of filling paste (Catalog of the products provided by BASF, www.basf.com)
Appendix C: Arc spray process

Figure A4. Pictures of arc spray system used in this project for deposition of alloy 625
Appendix D: Temporary surface burnout temperature indication

Figure A5. Shows the graphs resulted from TGA test conducted on Acrodur epoxy. The reaction peaks can be observed. The decomposition temperature and time were concluded from the results.

Figure A5. TGA results for Acrodur cured at 190, burnt in Air

Figure A6. Acrodur resin before burnout and after burnout in an alumina crucible and the TGA equipment used for testing the resin thermal properties
Figure A7. a) Acrodur resin before burnout, b) Acrodur resin after burnout, c) mixture of the alloy 625 powder and Acrodur resin after burnout
Appendix E: DVP-2000 system and the resulted graphs

Figure A8. DVP-2000 equipment console and sensing head

Figure A9. DVP-2000 sensing head monitoring the droplets characteristics during arc spray of alloy 625
Figure A10. Typical DVP-2000 monitoring results
Appendix F: TGA tests on foam samples

Figure A11. NETZSCH STA 449 F3 Jupiter TGA machine

Figure A12. Typical NETZSCH STA 449 F3 Jupiter TGA machine results for metallic foam samples
Appendix G: Adhesion test for arc sprayed deposits


The adhesion strength of the coated samples was measured using a PosiTest portable adhesion tester (Stone Tucker Instruments Inc.) based on the ASTM D4541-09 standard. E-6000 Craft Carded Adhesive was utilized to bond the adhesion test handles to the coating surface. The effect of different substrate roughness and various spraying distances on the adhesion strength of the coating skins to the foam core were examined.

![Adhesion test equipment and the tested samples that failed in different conditions](image)

Figure A13. Adhesion test equipment and the tested samples that failed in different conditions