The chemical vapor deposition technique for Inco nickel foam production–manufacturing benefits and potential applications

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Because of its versatility, the use of Chemical Vapor Deposition (CVD) techniques has increased considerably in the recent past. This is the technique adopted in the production of Inco nickel foams, in which nickel carbonyl is decomposed within a plater in the presence of a catalyst and a carrier gas. The nickel is deposited on a polyurethane (PU) foam substrate. The resultant foams are effectively replicates of the PU foam structure. The as-deposited nickel foams are sintered in a reducing atmosphere at high temperature to enhance ductility. In this paper, the capability of the CVD technique to produce uniform foams of different properties, with cell size ranging from ~450 to ~3200 μm, porosity from ~70 to ~98%, and nominal thickness up to 3 mm is presented. In addition to the established application as a battery electrode material, some other potential capabilities and applications are explored.

1 Introduction

INCOFOAM®[1] nickel foam - high purity nickel foam produced in a wide porosity range (~70% to 98% by volume) and based on the structure of reticulated polymer foams has been available for several years. In 2000, a new, large scale commercial production facility was commissioned at the Inco UK refinery in Clydach, near Swansea, Wales. A wide range of porosities and pore sizes, limited only by the availability of polyurethane foams, presents unique opportunities for custom-tailored properties to serve a variety of applications. Hybrid electric vehicles (HEV) for example, have attracted great public interest due to their energy savings and environmental benefit. High-quality Ni foam is used as the electrode material in HEV batteries. Applications of Ni foam in fuel cells and electrolyzers are under development. While rechargeable battery electrodes remain the dominant application at present, the material is finding its way into a host of new applications. This paper presents the industrial scale CVD process developed at Inco and its benefits in delivering high quality uniform Ni foam products. Applications of Ni foam in various fields are discussed based on INCOFOAM® nickel foam properties.

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[1] INCOFOAM® is a registered trademark of Inco Limited

J. Banhart, N.A. Fleck: *Cellular Metals and Metal Foaming Technology.* © MIT-Verlag (2003)

2 INCOFOAM® production process

To produce nickel foam, nickel metal is coated onto reticulated polymer substrates such as polyurethane foam and sintered afterwards to remove the polymer substrate in a controlled atmosphere at high temperature. In general, nickel coating can be applied by a variety of processes such as sputtering, electroplating and chemical vapor deposition (CVD) [1]. For mass production of continuous foam, electroplating and CVD are the main processes in the industry. The production process at Inco is based on CVD of nickel tetracarbonyl ($Ni(CO)_4$) onto open-cell polyurethane substrate [2].

$Ni(CO)_4$ was first synthesized in 1888 by Carl Langer and Ludwig Mond and since 1902 has been used commercially for the refining of nickel and the production of nickel powders and other special products. It has a boiling point of 43°C and is readily decomposed into elemental nickel and CO upon heating to 150 – 200°C via the following reaction:

$$Ni(CO)_4 \Rightarrow Ni + 4\ CO$$

The low decomposition temperature allows nickel deposition on temperature-sensitive materials, such as PU foam.

The commercial plating units at Inco semi-continuously produce coils of battery-grade foams approximately 2000 m long, 1 m wide and 1.3-3 mm thick in a single batch. The plating unit is essentially a cold-wall CVD reactor with a spool-to-spool winding mechanism designed to transport spooled, porous substrates through a series of deposition chambers under tightly controlled process conditions. The amount of nickel plated onto the substrate depends on plating gas composition, substrate temperature, substrate surface area, and residence time in the chamber. Typical deposition rate achieved in the current process is about 1 μm/min.

Following nickel deposition, the plated foam coils proceed to the heat-treatment operation. A typical coil of foam transported from the plating to sintering operation is shown in Figure 1 and illustrates the scale of this manufacturing process.

Figure 1

As-produced Ni foam coil shown in transit between plating and sintering operations

The most serious manufacturing challenge is presented by the highly toxic nature of the chemicals used in this process. Various engineering and procedural controls are in place to assure safe operation of the nickel deposition system.

Subsequent to the plating operation, the as-deposited foam, which still contains the polymeric substrate, is subjected to a high-temperature heat treatment in controlled atmosphere belt furnace. In the Inco process, the polyurethane foam burnout and high-temperature (~1,000°C) anneal of the nickel film are performed as a single step operation [3]. Figure 2 shows the onset of PU foam burn-out as the organic material escapes from the Ni shell under high pressure built inside the struts during the heat-up process. On the right, fracture cross-section of a hollow strut after high-temperature sintering is shown.

3 Nickel density range

The CVD process is unique in that it allows uniform 3-D distribution of nickel onto the polymer substrate over a very wide range of densities. Commercially available INCOFOAM® nickel foam densities range from ~0.2 to ~2.6 g/cm^3. Figure 3 shows three examples of achievable material porosity: ~98%, ~91% and ~74% by volume (0.2 g/cm^3, 0.8 g/cm^3 and ~2.3 g/cm^3, respectively) all deposited on the same PU foam. Thus the cell size is the same for each of these foams. The density difference is achieved primarily by adjusting the residence time (line speed) of the substrate inside the plating chamber. The material exhibits excellent 3-D uniformity of the Ni coating in the entire density range.

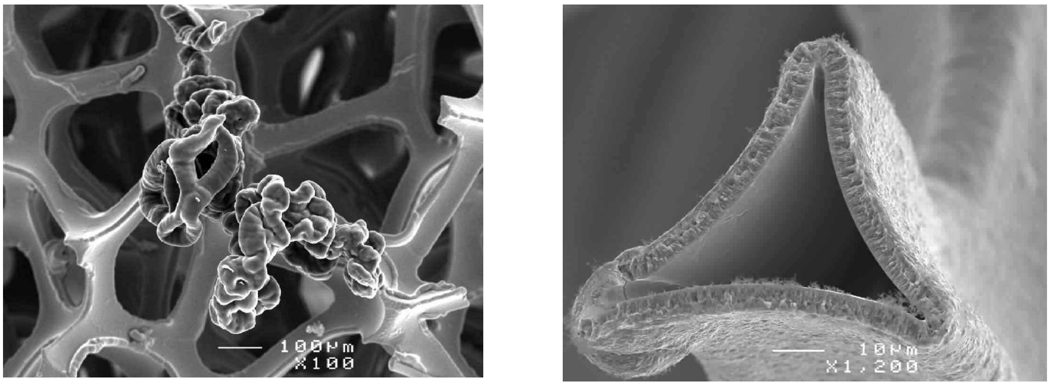
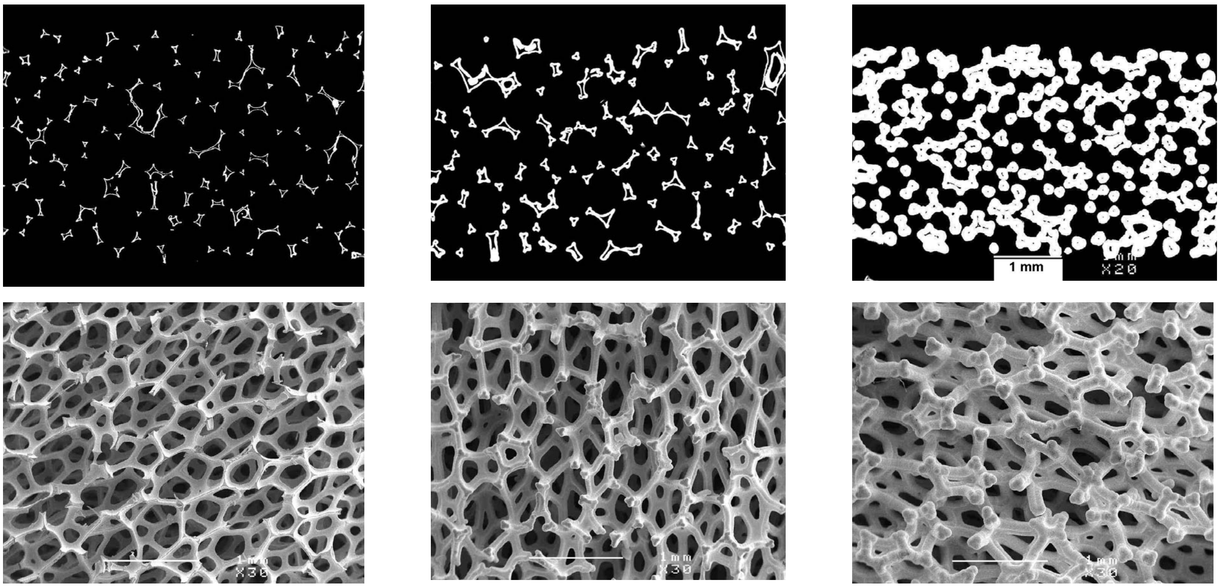


Figure 2 Polyurethane foam "eruption" from the as-deposited nickel foam during the burn-out process (left) and fracture cross-section of a hollow Ni foam strut after sintering (right)



0.2 g/cm3 (~98% porous) **0.81 g/cm3 (~91% porous)** **2.3 g/cm3 (~74% porous)**

Figure 3 SEM cross-sections and surface micrographs of several porosities INCOFOAM® nickel foam

4 INCOFOAM® pore size range

The pore size of INCOFOAM® nickel foam is determined by the pore size of the polymer foam template. Reticulated polyurethane foams are available in pore sizes ranging from about 5 ppi (pores per inch) to about 130 ppi (average 3-D cell diameter ~6 mm to ~0.4 mm). Examples of 110 ppi and 20 ppi foams are shown in Figure 4. Some anisotropy can be introduced due to the preferential stretch of the polymer during the early stages of metallization. Engineering techniques to control this parameter are under development.

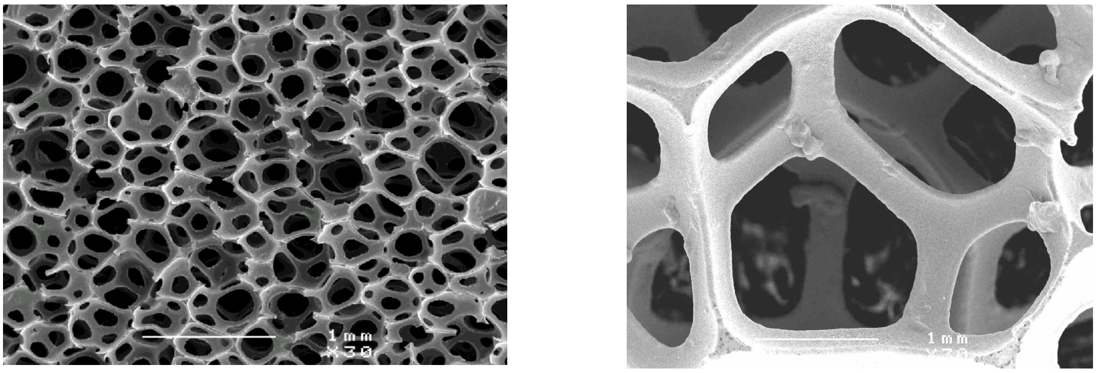


Figure 4 SEM images (both 30x mag.) of 110 ppi (left) and 20 ppi (right) foams

5 INCOFOAM® properties

5.1 Physical properties

A list of properties for three grades of INCOFOAM® nickel foam is shown in Table 1. The data are based on recent measurements performed at Cambridge and McMaster Universities. Note that some of the data are estimates based on both measured properties and established models for foam.

Property & units	**INCOFOAM® 0.19, 90 ppi**	**INCOFOAM® 0.20, 20 ppi**	**INCOFOAM® 1.7, 90 ppi**
Density, g/cm^3	0.18 - 0.20	0.19 - 0.21	1.69 - 1.71
Relative density, %/100	0.02 - 0.023	0.021 - 0.023	0.19 - 0.192
Cell size, mm	0.41 - 0.5	2 - 3.5	0.37 - 0.47
Anisotropy ratio, %/100	1 - 1.5	1 - 1.3	1 - 1.5
Young's Modulus (tension), Gpa	0.12 - 0.14	0.12 - 0.14	4.9 - 5.5
Young's Modulus (compression), Gpa	0.115 - 0.13	0.1 - 0.12	4.5 - 5
Shear Modulus, GPa *	0.042 - 0.048	0.04 - 0.043	1.8 - 2
Bulk Modulus, GPa *	0.1 - 0.2	0.09 - 0.11	4.2 - 4.5
Flexural Modulus, GPa *	0.12 - 0.14	0.11 - 0.13	4.7 - 5.3
Poisson's Ratio *	0.32 - 0.34	0.32 - 0.34	0.32 - 0.34
Elastic Limit (tension), Mpa	0.42 - 0.45	0.48 - 0.52	11 - 12
Elastic Limit (compression), Mpa	0.35 – 0.4	0.28 – 0.31	5.5 - 7
Ductility (tension) *	0.065 - 0.07	0.065 - 0.07	0.065 - 0.07
Densification Strain (compression)	0.6 - 0.62	0.5 - 0.55	0.3 - 0.32
Compressive Stress @ 25% strain, Mpa	0.42 - 0.45	0.52 - 0.55	17 - 18
Compressive Stress @ 50% strain, Mpa	0.59 - 0.61	0.58 - 0.62	35 - 38
Tensile Strength, Mpa	0.9 – 1.05	1.05 - 1.15	8 - 9.5
Modulus of Rupture, MPa *	0.42 - 0.45	0.48 - 0.52	11 - 12
Endurance Limit, MPa *	0.17 - 0.2	0.19 - 0.22	4.4 - 4.8
Hardness, MPa *	0.42 - 0.45	0.52 - 0.55	13 - 15
Energy Absorption at Densification, MJ/m^3	0.29 - 0.3	0.27 - 0.29	4.7 - 4.8
Fracture Toughness, $MPa.m^{1/2}$ *	1.55 - 1.75	1.6 - 1.8	10 - 16
Loss Coefficient *	0.02 - 0.03	0.02 - 0.03	0.02 - 0.03
Heat Deflection Temperature 0.45 MPa, K *	450 - 500	450 - 500	450 - 500
Melting Point, K	1720 - 1726	1720 - 1726	1720 - 1726
Maximum Service Temperature, K *	900 - 1100	900 - 1100	900 - 1100
Specific Heat, J/kg.K	452 - 460	452 - 460	452 - 460
Thermal Conductivity, W/m.K *	0.7 - 0.85	0.7 - 0.9	10 - 12
Thermal Expansion, $10^{-6}/K$	12.5 - 13.5	12.5 - 13.5	12.5 - 13.5
Latent Heat of Fusion, kJ/kg	280 - 310	280 - 310	280 - 310
Resistivity, 10^-8 ohm.m	850 - 950	700 - 900	68 - 73
Solid Density, Mg/m^3	8.88 - 8.92	8.88 - 8.92	8.88 - 8.92
Solid Young's Modulus, Gpa	210 - 216	210 - 216	210 - 216
Solid Elastic Limit, MPa *	100 - 120	100 - 120	100 - 120
Solid Fracture Toughness, $MPa.m^{1/2}$ *	80 - 90	80 - 90	80 - 90
Solid Maximum Use Temperature, K	550 - 600	550 - 600	550 - 600
Solid Thermal Conductivity, W/m.K	85 - 90	85 - 90	85 - 90
Solid expansion coefficient, $10^{-6}/K$	12.5 - 13.5	12.5 - 13.5	12.5 - 13.5
Solid Resistivity, 10^{-8} ohm.m	8.5 - 9	8.5 - 9	8.5 - 9

Table 1. INCOFOAM® physical properties [4]

*calculated values based on established models for metal foam

5.2 Impurities

Owing to the nature of nickel carbonyl processing, INCOFOAM® nickel foams exhibit very high chemical purity (>99.8% Ni). The as-deposited foam does contain higher levels of sulphur and carbon [5]. The sulphur is a by-product of the catalyst used in the nickel carbonyl CVD process, while the carbon arises as the PU foam starts to decompose at the plating temperature. However, both of these elements are largely removed during the sintering process. Thus, the final product contains only about 0.08% carbon and 0.02% sulfur by weight, respectively.

5.3 Density variation

The CVD process allows high degree of density control – both area-wise and across the thickness. Typical density variation of a 2,000 m long spool is less than 5%.

6 New applications potential

Nickel foam possesses unique features such as exceptional uniformity, light weight, high porosity, intrinsic strength, corrosion resistance, and good electrical and thermal conductivity. Various applications are discussed below.

6.1 Battery electrodes

Ni foam has been predominantly used in battery electrodes, especially for NiMH batteries. Such rechargeable batteries have found applications extensively for portable computers, cellular phones, battery-powered scooters, bicycles and hybrid electric vehicles. The CVD-derived INCOFOAM® nickel foam provides uniform compressibility of the electrode, allowing use of very light weight structures in electrode manufacturing. Effective surface area of the electrode active materials could thus be increased to enhance the high power capability. The uniform structure has now been extended to a wide range of specifications including 0.2 – 2.6 g/cm^3 densities and 450 to 3200 μm pore sizes foams.

6.2 Fuel cell applications

Ni is active in hydrogen dissociation at elevated temperatures. This makes Ni foam a potential material as an electrocatalyst in molten carbonate fuel cells (MCFC), which normally operate at 550-700ºC. Chemical environment of MCFC fuel cells is such that nickel can be used for both electrodes. INCOFOAM® nickel foam with wide range of density specifications provides a good structure for these applications as it offers high porosity, good gas distribution characteristics and thermal stability.

Ni foam may find applications as bipolar plate enhancement material for proton exchange membrane fuel cells (PEMFC), electrode interconnectors for solid oxide fuel cells (SOFC), and electrode materials in electrolysis such as hydrogen electrolyzers. It may also be enhanced in surface area for potential use in steam reforming reactions to supply hydrogen or syngas for fuel cells.

6.3 Catalyst materials

Due to the unique open cell structure, low pressure drop, intrinsic strength and resistance to thermal shock, Ni foam has potential as a catalyst support for automotive catalytic converters and catalytic combustion, and for catalytic filters for diesel engine particulates. Its high thermal conductivity may be superior to ceramic monolith supported catalysts in low light-off conversion of carbon monoxide and hydrocarbons during engine cold start. In this sense, Ni foam may be comparable or superior to high temperature steels as catalyst supports. Other catalyst applications of nickel foam may include foam supported catalysts for Fisher-Tropsch reaction, steam reforming and hydrogenation of fine chemicals.

6.4 Other opportunities

Owing to its uniform 3-D structure with custom porosity, INCOFOAM® nickel foam may find applications as a filter material. Its magnetic properties may make it suitable as a magnetic flux conductor for handling magnetic particles in a fluid. Other applications may include hydrogen storage medium, heat exchanger medium, and even in arts owing to its unique shaping capabilities, wide porosity range and environmental stability.

6.5 Use of CES in Application Selection: A Case Study

For all new materials there is a need to search for potential applications beyond those for which the material was originally developed. We have found that the Cambridge Engineering Selector (CES) is a valuable tool in the search for new applications [6]. CES enables one to compare materials indexes for a wide range of materials on a single chart.

Applications such as catalytic converters and steam reformers require porous structures that transmit gas at high rates while also managing the thermal load on the structure. As the rate of gas flow through the structure increase the pressure drop across the structure rises and this can limit some applications [6]. The pressure drop depends on a number of factors including the properties of the fluid being transported. In terms of the foam however it depends only on the geometry of the foam and scales as $a^{-1.4}\rho^{-0.2}$, where a is the cell size and ρ is the foam relative density. We use a materials index $M = a^{1.4}\rho^{0.2}$. Heat transfer through the cell walls is maximized using another materials index, namely, $\lambda\rho^{1/2}$ where λ is the thermal conductivity of the foam. A selection chart for this application is shown in Figure 5. This chart displays data for all foams and honeycombs; however, the data has been faded for all materials except open-cell foams since an open structure is required by this application. It shows that high density INCOFOAM® nickel foam offers interesting properties, especially when heat transfer requirements are dominant in the application of interest.

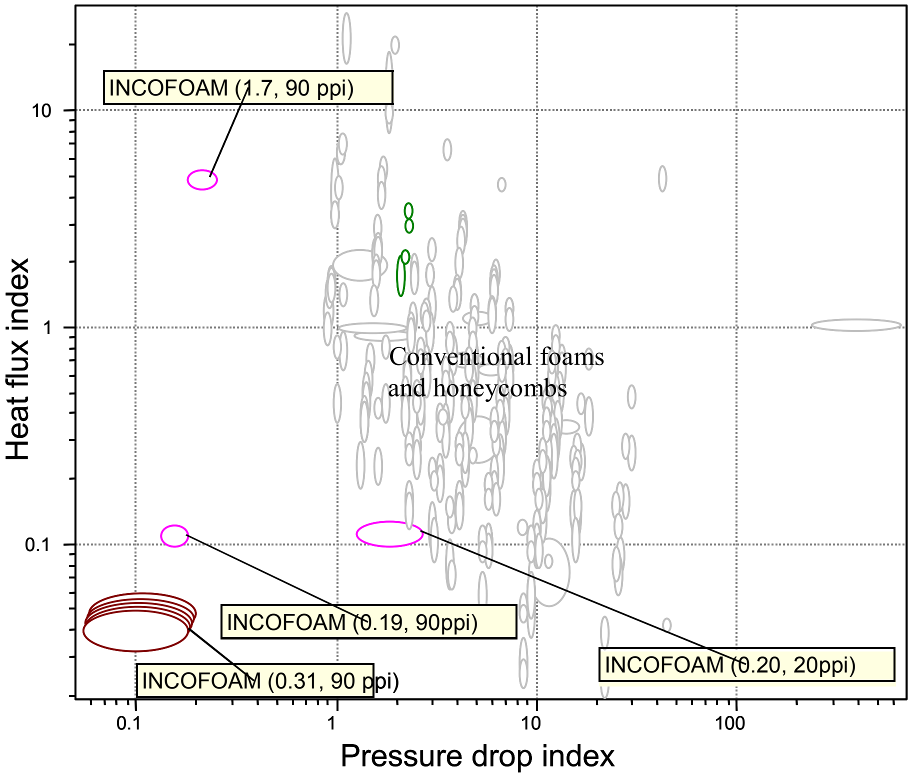


Figure 5 Materials selection chart for foams using indexes of interest for catalyst and steam reformer applications. Material designations (e.g. 1.7, 90 ppi) refer to 1.7 g/cm^3 apparent foam density and pore size grade of 90 pores per inch.

7 Summary

INCOFOAM® nickel foam produced by the Inco CVD manufacturing process possesses superior uniformity and mechanical properties and represents a unique material in the field of metal foams. INCOFOAM® nickel foam products with a wide range of specifications (density 0.2 – 2.6 g/cm^3 and pore size 450 - 3200 µm) are now produced on a mass scale and are commercially available for customer exploration. Ni foam has found a predominant application as a battery electrode, but shows good promise for use in a variety of other applications.

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