

Figure 4: Printed organic solar cell where each of the layers has been printed, including the metal electrodes.

active device and e) high charge mobility. Modification of each of these properties is readily achieved with organic molecules, the challenge is to match the properties in one material.

Control of thin film morphology has been our starting point for the

development of new materials. Hexa-perihexabenzocoronenes (HBC) stack to form extended structures and were an ideal building block for modification.

Addition of dioctylfluorene (F8) groups gives a solution processable material, which can be formulated as an ink for use in solar cells. When pure bis-F8HBC is melted and forced through a die the fibres are made up of a hexagonal arrangement of bis-F8HBC nano-wires as can be determined from Wide Angle X-Ray analysis, Figure 3. The stacking gives good charge transport and is maintained in blends with PCBM as we have seen from X-ray diffraction results for thin films.

We have recorded solar cell efficiency of these systems of up to 2.5%, which remains low compared to traditional solar cells, however there is an enormous ability to modify the current systems to improve efficiency. HBCs are one of many materials being developed in our current program. Recent grants from the Victorian Government DIIRD SPF fund (\$5.0 million), Victorian Government DPI SERD2 (\$1.76 million) with matching funding from the Australian solar Institute (\$1.76 million) will help dive efficiencies to a commercially relevant 10%, improve durability and bring these systems to a pre-commercial product. The development of Organic Solar Cells requires input from many fields and is impossible without the input of the many experts found within our team and those of our partners at CSIRO MSE and Monash University.

Each layer of an Organic Solar Cell and the interface interactions are all targets of intense research, finding the perfect combination and translation of this to an industrial process is the current goal of our research program. The end result is a solar cell in which each layer can be printed.

# FEATURE

# **Corrosion Protection with the Dymet Coatings**

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Low Pressure Cold Spray also known as Dynamic Metallisation (Dymet) is one of the thermal spraying techniques that enables the deposition of anti-corrosive coatings. The Dymet equipment is a flexible and cost-effective tool used in both large manufacturing plants and small repair shops. This article provides the test results of the Dymet coatings and demonstrates their suitability for corrosion protection in various industrial applications.

#### Key words: Dynamic Metallisation, Dymet, Low Pressure Cold Spray, Corrosion protection, Industrial applications

Thermal spray techniques have been used for deposition of anti-corrosion coatings in Australia and New Zealand for more



Figure 1 Dymet model 413

than 35 years (Abraham and Sathasivam, 1998). The typical materials for protective coatings are zinc, aluminium and zincaluminium alloys (Leclercq 1980: Sulit, 1993). The durability of such coatings has been documented in various publications. Thus, low-carbon steel panels coated with zinc and aluminium by thermal spraying were exposed to various aggressive environments such as seawater, rural, industrial, salt air, and salt spray (Longo and Durmann 1978). The results indicate that the coatings can protect steel products in the corrosive media for more than 19 years.

Low Pressure Cold Spray also known as Dynamic metallisation (Dymet) is the one of the thermal spraying methods able to deposit anti-corrosive coatings. A number of original ideas and technical solutions realised in the Dymet technology have been protected by the patents in many countries (Kashirin et al., 1997, 2002 and 2004). The main principle of this method is to utilise compressed air to carry and deposit fine metal particles on the surface of a substrate. Due to high velocity of the metal particles accelerated in the specially designed spraying gun, they adhere to the substrate on a subatomic level and create a continuous metal layer.

We have previously reported on some aspects of the Dymet technology (Spiridonov 2004 and 2006; Luzin 2009). This article provides information on the mechanical properties of the Dymet coatings as well as their corrosion resistance.

#### Mechanical Properties of the Dymet Coatings

The Dymet coatings are characterised by a combination of valuable properties such as high adhesion to substrate, great mechanical properties, low porosity and gas permeability, increased hardness and corrosion resistance. Some of these characteristics are described below.

The adhesive strength (adhesion, bonding strength) of a coating with a substrate is one of the most important parameters. Typical adhesion of thermal coatings ranges between 10-20 MPa (electroarc metallisation) and 90-100MPa (a detonation method). During the development of various Dymet coatings a large amount of measurements and tests of the coatings was conducted. The experimental data of adhesion tests of some types of the coatings were generalised (See Table 1).

The tests results show that the Dymet coatings adhesion is within the range of 40-80 MPa. In some cases it may reach 100 MPa. It can be noted that aluminium coatings usually have superior bonding strength with all types of substrates compared to the coatings of other metals, obtained in similar conditions.

During the adhesion pin tests it was observed that the samples fracture mainly not by the interface between the coating and substrate, but in the volume of the coating. It can be characterised as a cohesive fracture rather than an adhesive one. This fact was confirmed for various types of coatings and shows that mechanical strength of the coatings is comparable with their adhesive strength and lays in the range of 30-80 MPa.

Another significant coating characteristic is its hardness. The Dymet equipment is used to deposit mainly soft metals such as aluminium, zinc, copper and their mixtures. At this stage the hardest commercial material is nickel powder. However, it was noticed that due to the presence of ceramic particles the Dymet metal coatings are generally harder than the same solid metal.

To develop harder coatings for various applications we investigated the addition

of a chrome powder to nickel and zinc powders. A comparative study of hardness of commercial and modified powders has been conducted. Due to the fact that the hardness may vary with a load and be influenced by surface scratches and roughness two plates were used as references - a stainless steel plate and a mild steel plate. The Brinell hardness test (Australian Standard 2007) was conducted with a 2mm ball indenter and a 40kg load. The Vickers test (Australian Standard 2003) was conducted with a prism indenter and a 50kg load. The hardness test results are given in Fig. 2.

Fig. 2 shows that the nickel and nickelchrome coatings are comparable or better than stainless steel. They reach 180-190 BHN and 230-250 HV. All nickel and nickelchrome coatings are harder than mild steel. It was noticed that adding zinc powder to nickel compounds improves the powder deposition rates but significantly reduces their hardness.

#### **Corrosion resistance**

To test the corrosion resistance of Dymet coatings a 168-hour salt spray test (Australian Standard 2001) was conducted by a NATA accredited laboratory. The Dymet coatings were compared to two hot dip galvanised parts. The thickness of the Dymet coatings was 40-50 microns, zinc galvanised layer – 30-50 microns. The salt spray test results (See Table 2) show that the sprayed coatings are equal or better than zinc galvanised coatings. The best results were achieved with a nickel-zinc compound. The samples after the salt spray test are shown in Fig. 3. It can be seen that the unprotected steel plate became completely rusty after the test. The red rust bleeds through the commercial galvanised parts (#6 and 7). The samples #2-5 coated with various Dymet coatings show no corrosion, except the side edges that were not coated at all. The best results were achieved with the nickel-zinc coatings which lasted twice as long as the galvanised parts.

#### **Industrial Applications**

The corrosion test results demonstrated the suitability of the Dymet coatings for corrosion protection of metal parts and structures. In particular they can be used in the following applications:

- > protection of welding seams, buildings and metal structures,
- restoration of zinc galvanised layers after welding,
- elimination of galvanisation defects on hot dip galvanised structures,
- restoration and corrosion protection of worn automotive parts and bodies,

Due to their high durability the nickel based coatings can be recommended for heavy duty applications. In particular they can be used to protect the metal structures working in humid areas, near the costal line, or in contact with corrosive chemicals; parts of the sea boats and submarines; components of the drilling platforms and similar.

### Table 1: Adhesion strength of some Dymet coatings on aluminium and steel substrates

Powder composition	Substrate material	Surface preparation	Adhesion, MPa
Al, $Al_2 O_3$	Aluminium	-	60-90
$AI, AI_2O_3$	Steel	Sand blasting	40-60
Al, Zn, $Al_2O_3$	Aluminium	-	60-80
Al, Zn, $Al_2O_3$	Steel	Sand blasting	40-60
Al, Zn, $Al_2O_3$	Ceramic	Sand blasting	10-30
$Zn, Al_2O_3$	Steel	-	15-20
$Zn, Al_2O_3$	Steel	Sand blasting	30-50
$Zn, Al_2O_3$	Steel	-	40-50
Ni, Zn, $Al_2O_3$	Steel	Sand blasting	30-50
Ni, Al <sub>2</sub> O <sub>3</sub>	Aluminium	No	40-50

## FEATURE



Figure 2 Brinell and Vickers hardness of the Dymet coatings in comparison with stainless and mild steels

More details about the Dymet typical applications can be found in our previous publications (Spiridonov 2004 and 2006).

This article provides information on the mechanical properties and corrosion resistance of the Dymet coatings. The salt spray test results show that the sprayed coatings are more durable than industrial zinc galvanised parts. The Dymet coatings can be recommended for various industrial applications including heavy duty anti-corrosion protection and marine protective applications. The combination of technical and economic features of the Dymet equipment such as low cost, environmentally friendly spraying process, portability and operational flexibility makes it attractive to the customers.

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Australian Standard AS 1817.1 - 2003 Metallic materials - Vickers hardness test -Test methods (ISO 6507-1:1997, MOD)



Figure 3A The sample from left to right after the salt spray test

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Figure 3B The samples 6 and 7 after the salt spray test

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#### Table 2 Results of the neutral salt spray test

Sample #	Sample	Hours	Observation	Further effect
1	Steel substrate with no coating	72	Significant amount of red rust	Significant degradation
2	Zinc coating	118	Trace amount of red rust noted	Slight increase in red rust
3	Nickel- Zinc coating	144	Trace amount of red rust noted	Slight increase in red rust
4	Alum- Zinc coating	72	Trace amount of red rust noted	No increase in red rust
5	Aluminium coating	72	Trace amount of red rust noted	No further red rust noted
6	Hot dip galvanised part 1	96	Red rust noted	Slight increase in red rust
7	Hot dip galvanised part 2	72	Red rust noted	Slight increase in red rust