Enhancement of adhesion strength of thick copper coatings on used nuclear fuel steel containers prepared with the forced pulsed waterjet (FPWJ)

A. Nastic, B. Jodoin, R. Fernandez, D. MacDonald

Department of Mechanical Engineering, University of Ottawa, Canada

M.Vijay, A. Tieu, W. Yan, B. Daniels, M. Xu

VLN Advanced Technologies, Canada

ABSTRACT

Canadian nuclear power generator industry reportedly has nearly 2 million fuel rod bundles being held in above ground water-cooled reservoir awaiting for safe and permanent methods of underground storage. The Nuclear Waste Management Organization (NWMO) proposed an encapsulation storage design concept using thick carbon steel pods filled with spent nuclear fuel rods permanently sealed and encased in bentonite clay to be stored deep underground in controlled repository sites. To protect the steel pods from environmental corrosion, pure copper coating applied by Cold Spray technology can be used, which has key technical and financial merits over other possible coating processes. Conventional surface preparation method (grit blasting) leads to reduced coating adhesion and potential delamination. However, Forced Pulsed Water Jet (FPWJ) surface preparation delivers a much more intricate surface topography that enables copper coatings to effectively bond to carbon steel without any foreign media contamination. The paper will discuss the various coating/substrate bonding mechanisms through experimental work.

1 INTRODUCTION

The Cold Spray process was discovered in the mid-1980s at the Institute of Theoretical and Applied Mechanics at the Siberian Division of the Russian Academy of Science in Novosibirsk (1). A variety of metallic, polymer and composite particles were successfully deposited onto a wide range of substrate materials. The process is now part of the thermal spray process family but its operating characteristics are very unique. In Cold Spray, inert gas is accelerated through a De Laval nozzle to supersonic velocities, as shown in Fig.1. As it expands in the diverging section, the gas cools down. The coating material is injected in the high velocity stream either prior to the throat or downstream in the diverging section, in the form of powder ranging in size from 5 to 100 μm (1), (2). Accelerated by the gas stream, the particles are propelled towards the substrate surface. As they impact the substrate, the particles undergo a high strain rate deformation process. A bond between the particle and the substrate is created only if the particles impact at a so-called critical velocity that is material property dependant (3). As particle deposition continues, a coating is thus generated.

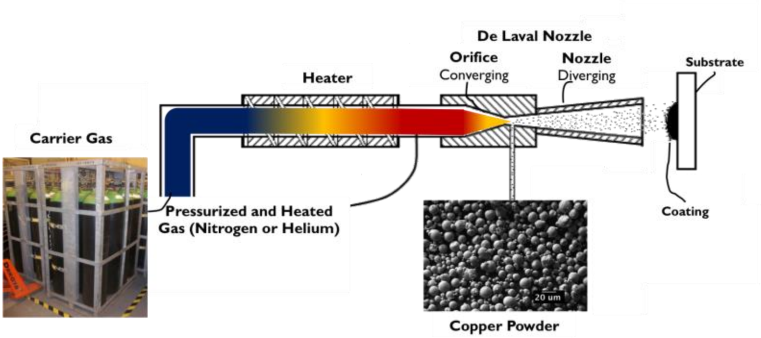

Fig.1. Cold Spray process.

As opposed to the other thermal spray processes, the gas is preheated to temperatures below 1100 °C before entering the nozzle. Due to the fast cooling of the gas during the expansion process, the particles never reach their melting point making the Cold Spray a solid-state deposition process (4). Drawbacks related to the material melting encountered in thermal spray processes such as material oxidation, phase transformation and tensile residual stress build up are thus avoided (4).

In recent years, the development of the Cold Spray technology has enabled its use in multiple industry sectors as a reliable and efficient coating process. As an example, the process is being considered as a valuable contender for the deposition of a thin copper coating layer for Canada’s nuclear reactor spent nuclear fuel rods sealing system (5). Over 2 million used fuel bundles have been produced over the last decade and only recently has Canada established its solution for the long term, safe and secure management of the radioactive fuel (6). The main goal of the long term containment of the spent nuclear fuel is to safely contain and isolate used nuclear fuel in a deep underground repository, in a suitable rock formation. The sealing system needs to provide physical and chemical environment that will constrain any possible radionuclides mobility under certain unforeseen conditions that would diverge from the excepted normal evolution of the repository (5), (7)–(9). As opposed to existing designs used in Europe that use a thick sleeved copper shell (8)–(11), the Canadian containment system will include an integrated thinner (4mm thick) copper coating. The sought characteristics of the fuel container design are corrosion resistance, compatibility with the neighbouring sealing material such as bentonite clay (8), (9), mechanical strength and capacity.

The Cold Spray process is being considered as a coating solution since copper deposition onto steel containers could be done at low temperatures to limit copper oxidation, while keeping high deposition rates with high deposition efficiencies (12), (13). Previous studies have shown that copper deposition onto steel is challenging to achieve due to the low material metallurgical compatibility. While it is possible to get some copper deposition onto steel, the adhesion during the coating build up process becomes an issue and presents a serious challenge (14). Many have attempted to vary the spray parameters and change the particle characteristics (size distribution, oxide content, geometry, etc.) but all have resulted in coating delamination during deposition (15).

An innovative two-step approach has been proposed where a first thin copper layer is applied using helium and the rest of the coating thickness is generated using nitrogen (8). Helium allows the particles to reach higher impact velocities, which leads to increased particle and substrate deformation. The deformation promotes mechanical interlocking and consequently higher coating adhesion strengths are achieved. While this method results in successful copper coating deposition and build-up, the use of helium is not ideal as it is a non-renewable resource and substantially more expensive than nitrogen.

The current study focuses on exploring new possibilities to deposit a copper coating onto a steel substrate using only nitrogen by evaluating and developing a new substrate surface preparation method that would promote mechanical anchoring and consequently increase the coating adhesion strength and prevent delamination (16). The traditional grit blasting method extensively used in thermal spray processes can only produce roughnesses (Ra) of less than 10 μm at the highest parameters (17), (18). As this roughness might not be enough to promote coating adhesion, this work will evaluate the benefits of using the novel forced pulsed waterjet (FPWJ) technique to generate large substrate roughnesses and assess its effect on the coating adhesion strength.

The force pulsed water jet (FPWJ) surface preparation process uses a piezo-electric transducer at 40 KHz to create ultrasonic vibrations. These vibrations modify a pressurized water stream to transform it from a continuous to a pulsed waterjet. The high pressure and high frequency water stream rapidly loads and unloads the substrate surface locally causing its failure through cyclic fatigue loading (16), (19), (20). The erosive capacity of the stream is caused by the generated water hammer phenomenon that develops at the surface. An intricate surface topography is created by such substrate surface treatment. Controlling the process parameters can vary the final surface roughness (16).

2 EXPERIMENTAL PROCEDURES

2.1 Cold Gas Dynamic Spraying – CGDS

In this work, the coatings have been produced using a commercially available EP Series SST Low Pressure Cold Spray system (Centerline (Windsor) Ltd. Windsor, Ontario, Canada). A De Laval nozzle having a throat and exit diameter of 2 mm and 6.6 mm respectively along with a diverging section length of 120 mm has been used. The spray parameters used for the copper deposition are presented in Table 1. For consistency purposes, samples were sprayed individually and were thermally insulated using a high temperature (polybenzimidazole) holder. Prior to the adhesion test, once deposited, the coating surfaces have been machined flat and down to a total thickness of 600 μm.

Table 1. Cold Spray Deposition Parameters

Parameter	Value
Gas Temperature	500 °C
Gas Pressure	3.8 MPa
Gas Nature	Nitrogen
Feed Rate	35 g/min
Traverse Speed	25 mm/s
Standoff Distance	10 mm

2.2 Substrate Material Selection

Low carbon steel A519 Grade 70 has been selected in this study as the substrate material. Flat 38mmx38mmx25.4mm rectangular substrates have been used for preliminary deposition analysis to examine the coating/substrate interface characteristics. In addition, following the ASTM-C633 coating adhesion strength standard, the substrate material has also been machined into 25.4 mm diameter and 38 mm long cylinders. A gas atomized spherical pure copper powder having an average particle diameter of 8µm (CU-159, Praxair surface technologies) has been used to produce the coatings.

2.3 Substrate Characterization

Each substrate roughness has been evaluated using a digital microscope (VHX – 1000, Keyence Corporation, Osaka, Japan) through a 3D depth composition stitching process. The generated 3D surfaces have then been converted to x-y-z coordinates values and transferred to a Matlab program for the calculation of the representative root mean square roughness value (Rq). Cross-sections of the depositions have been produced and the coating/substrate interface was analysed using an SEM (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany).

2.4 Substrate Preparation

Multiple surface preparation methods have been used to prepare the substrate surfaces. A polishing method characterized by a 3 µm particle fluid suspension final step has been used to create a mirror finish surface. A gravity fed grit blasting system has been used to generate surfaces with small roughnesses. Ferrosilicate grits having an average diameter of 850 µm were propelled through a steel nozzle at 400kPa and at an angle of 45°. Finally, the FPWJ technique was used to create six different high surface roughnesses. The FPWJ general parameters used to prepare the surfaces are presented in Table 2. As shown, the nozzle velocity has been varied between 160 mm/s and 600 mm/s to generate different and uniform surface topographies.

Table 2. FPWJ Substrate Preparation Parameters

Parameters	**Value**
Water Pressure	69 MPa
Pulse Frequency	40,000 Hz
Nozzle Diameter	1.4 mm
Stand Off	2
Step Index	0.1 mm/pass
Sample	**FPWJ Nozzle Velocity (mm/s)**
FPWJ-1	600
FPWJ-2	500
FPWJ-3	420
FPWJ-4	350
FPWJ-5	290
FPWJ-6	160

2.5 Adhesion Strength Testing

Three samples per surface preparation methods have been tested in compliance with the ASTM C633 standard to evaluate the coating adhesion strength. A thermally cured elastomeric bonding agent (FM-1000, Cytec Engineering Materials) with an adhesive strength of 76.9 MPa has been used in this study to glue the coated substrate with a counter cylinder. The tests were performed using a universal tensile machine.

3 RESULTS AND DISCUSSIONS

3.1 Substrate Roughness

The resulting surface roughness values obtained using the methods presented earlier are found in Table 3. The quadratic mean roughness values range from less than a micron to values above 105 µm using the polishing method and FPWJ surface treatment respectively. The grit blasting process generated an average roughness of 6.7 µm.

Table 3: Roughness Values and Adhesion Strength for each Substrate Preparation

Sample	Roughness Rq (µm)	Adhesion Strength (MPa)
Polished	0.9 ± 0.3	0.0 ± 0.0
Grit	6.7 ± 0.2	0.0 ± 0.0
FPWJ-1	22.2 ± 1.3	28.2 ± 7.2
FPWJ-2	41.6 ± 2.7	49.0 ± 5.8
FPWJ-3	57.1 ± 4.2	53.2 ± 4.3
FPWJ-4	73.9 ± 2.2	56.5 ± 2.5
FPWJ-5	80.1 ± 1.2	53.4 ± 5.3
FPWJ-6	105.2 ± 4.9	51.1 ± 6.3

Fig. 2 shows the resulting surfaces topography, prior to the coating deposition process, for all three methods used. Fig. 2a depicts the polished surface morphology, which shows minimal surface roughness. Fig. 2b exhibits the general surface structure for the grit blasted samples, where slight material flow, caused by surface shear during grit impact, is seen. The FWPJ-2 sample surface is depicted in Fig. 2c. Large intricate features are created during the FPWJ treatment, which potentially serve as anchoring points during the coating deposition. The surface was analysed at larger magnifications and Fig. 2d shows the details of such analysis. Micron and sub-micron features are observable on the FPWJ treated surface.

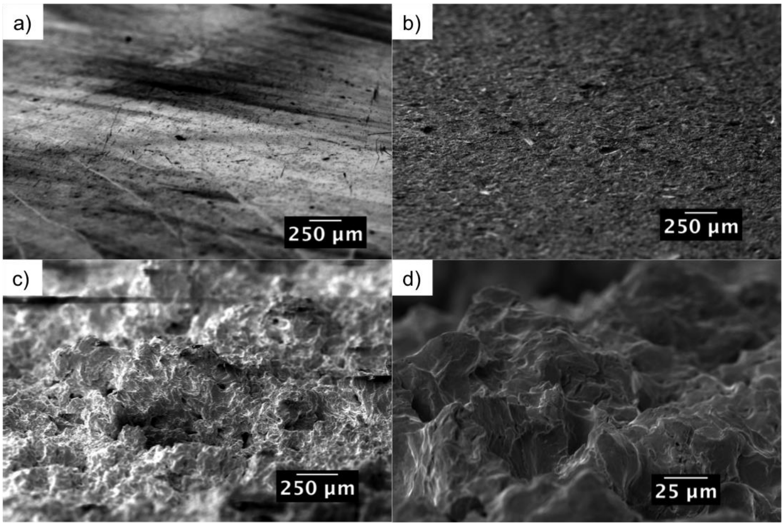

Fig. 2. Substrate surface topography obtained using different surface preparation methods; (A) polished, (B) girt blasted, (C) FPWJ-2, and (D) FPWJ-2 details.

3.2 Coating Characteristics and Adhesion Strength

As previously shown in other studies (21)–(23), the deposition of copper onto steel is expected to form very low to none metallurgical bonds. In this study, during the deposition of copper onto the polished and grit blasted samples, the coating has delaminated either during the coating build-up process or after the deposition. All delaminated coatings were curved with the center protruding outwards, which tends to indicate the presence of compressive residual stresses. The coating detachment during deposition could be caused by the stress accumulation at the interface with coating thickness, which once reaching a critical value causes delamination of the coating. Thus, the low adhesion of the coating sprayed on substrates with low roughness is unable to overcome this residual stress build up.

All coatings deposited on FPWJ treated surfaces have adhered properly during and after deposition. This result is novel, as no successful deposition using exclusively nitrogen has ever been reported previously. All attempts of deposition have always resulted in coating delamination. The successful coating adherence achieved in this study using nitrogen and low spray parameters is a first for the corresponding material combination. Fig. 3 shows the coating/substrate cross-section interface for different substrate roughnesses. The copper particle high deformation process during impact leads to highly dense coatings as seen in Fig.3. Moreover, the particles sufficiently deform to properly fill intricate substrate crevices found on the FPWJ treated surfaces. Those complex features play a major role in the coating adhesion strength as they provide mechanical anchoring points to the coating. The interlocking obtained through macro and micro surface features is sufficient to overcome the residual stress present at the interface and provide enhanced adhesion strength to the coating. The resulting coating adhesion strengths obtained for the coating sprayed on the various FPWJ treated surfaces are presented in Table 3 and in Fig.4.

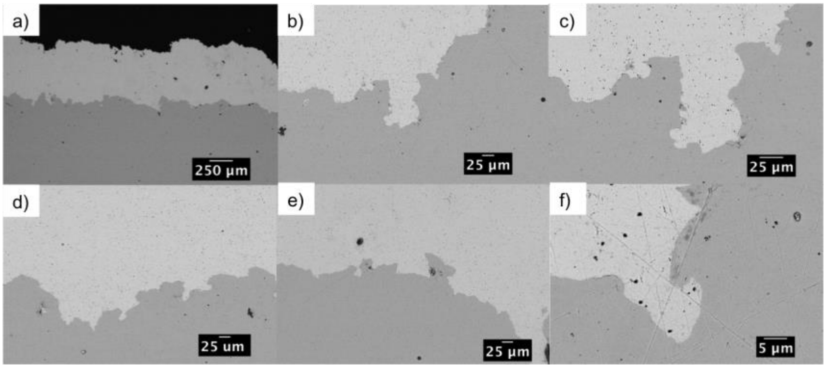

Fig.3. Cross-sections of coating/substrate interfaces at different magnifications; (A) (B) (C) are FPWJ-2 and (D) (E) (F) are FPWJ-5 samples.

As previously mentioned, coatings deposited on polished and grit blasted surfaces have delaminated prior to the adhesion test, thus resulting in zero coating adhesion strength as shown in Fig. 4. For FPWJ substrates, the coating adhesion strength increases with increasing substrate roughness up to approximately 55 MPa before reaching a plateau at a roughness of 60 µm. During adhesion tests, all tested coatings have failed in pure adhesion at the coating/substrate interface.

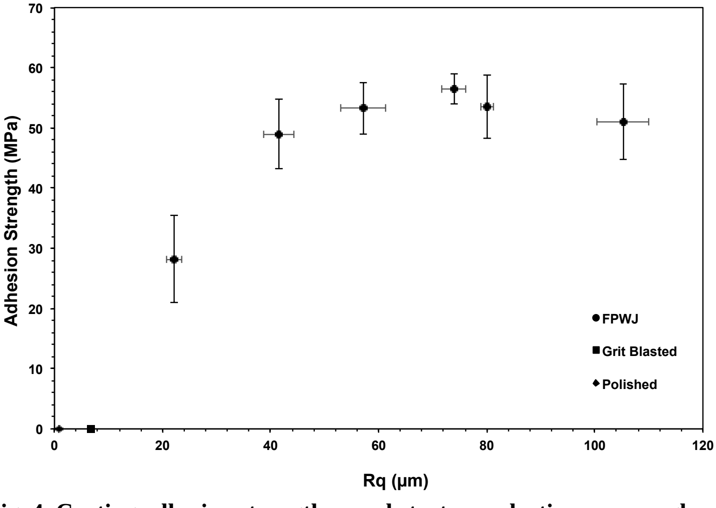

Fig. 4. Coating adhesion strength vs. substrate quadratic mean roughness.

The copper/steel couple material is not chemically compatible to create metallurgical bonding during low parameter deposition using nitrogen (21)–(24), which explains the constant coating delamination obtained on low substrate roughnesses. The incompatibility has been proven in other studies for other types of high strain deposition processes (21), (24). The difficulty achieving metallurgical bonding along with the results of the current study leans to indicate that the copper coating adhesion strength obtained is exclusively attained through mechanical anchoring mechanisms. The lack of hooks on the polished and grit blasted samples could explain the lack of coating adhesion strength. An increased amount of hooks evidently increases the amount of mechanical anchoring points and consequently the resulting coating adhesion strength.

Fig. 5 shows the fracture surface of both the coating and substrate after the adhesion test. Some copper particles have remained on the steel substrate anchoring regions after the coating has failed in adhesion. The coating surface, shown in Fig.5b, shows evidence of ductile deformation resulting from the pulling during the adhesion test. These results indicate that the adhesion at the interface is of mechanical type while the bonding between the particles is metallurgical.

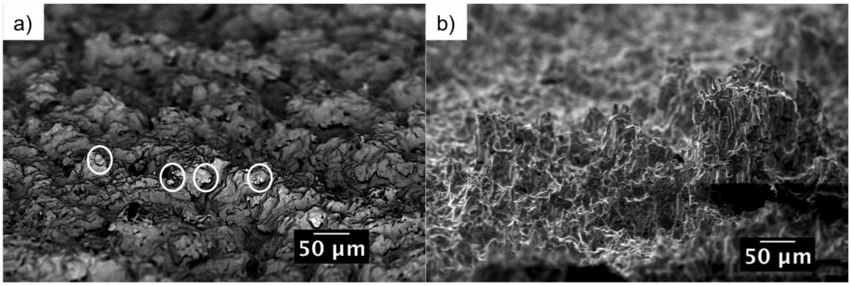

Fig.5. Fracture surface topography of the FPWJ-2 sample; (A) substrate side and (B) coating side. Copper residues that remained on steel surface are circled.

The association of the coating adhesion strength to the number of substrate anchoring points correlates well with previous results presented in the literature for the deposition of copper onto steel using helium as the propelling gas. Since particles reach higher velocities when deposited using helium, the substrate is capable of deforming during particle impact, which creates intricate substrate surface features.

4 CONCLUSIONS

This study has focused on the deposition of copper coatings on steel using the cold spray process and exclusively nitrogen as the propelling gas. It has evaluated the benefits of using the FPWJ surface preparation procedure to develop adhesion between the coating and substrate and eliminate the delamination problems that typically occur when depositing copper on steel using nitrogen. Substrate surfaces have been prepared through polishing, grit blasting and FPWJ methods to generate and evaluate a wide range of substrate roughnesses and topographies. The thick copper coatings produced were all dense and adhesion tests on successfully adhered coatings have been performed following the ASTM C633 standard. Coatings deposited onto substrate treated using the classical preparation methods have all delaminated prior to the adhesion tests. Coatings have successfully adhered only on the FPWJ prepared surfaces. It was demonstrated that the intricate features created through the FPWJ process provides mechanical interlocking to the coating allowing to reach high adhesion strengths during testing.

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