Transactions of the Korean Nuclear Society Autumn Meeting
Gyeongju, Korea, October 29-30, 2015

Coating Properties of WC-Ni Cold Spray Coating for the Application in Secondary Piping System of Nuclear Power Plants

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1. Introduction

Due to economical benefits, carbon steel is used in secondary water chemistry environment at nuclear power plant even though it has poor corrosion resistance when exposed to the environment [1]. Especially, secondary water chemistry environment is distinguished from general environment including fast flow, high pH, dissolved oxygen control and high pressure leading to wall thinning of pipe increasingly named as the flow accelerated corrosion (FAC) [2]. As a result of FAC, severe accidents, failure of carbon steel like a Mihama Unit-3 occurred.

Chemical composition change of carbon steel or coating to inner surface is one of methods to improve corrosion properties. Among them, thermal spray coating is convenient solution to apply at industry. Powder is melted at blast furnace and ejected to substrate. After adhesion, substrate and coating layer is cooled down and coated layer protects steel from corrosion finally. However high thermal energy is transferred to substrate and coating layer so it leads high thermal residual stress in coating procedure. Besides, high temperature for melting powder makes unexpected chemical reaction of powder like an oxidation or carburization [3-5].

Whereas, cold spray uses low temperature comparing with other thermal spray. Thermal energy is used for not melting powder but high kinetic energy of powder and plastic deformation during collision. Therefore, fuel such as oxygen-acetylene gas is not needed. It needs carrier gas, compressed air, nitrogen or helium, to increase kinetic energy of powder and move powder to substrate. Moreover defects of powder are not happened and fewer residual stress is in coating because of low temperature [3].

Tungsten carbide (WC) is cemented carbide and has high wear resistance and corrosion resistance at acidic solution [5, 6]. However coating using WC is difficult due to high melting temperature. In thermal spray, minimum temperature is 3000K so melting temperature of WC is not a problem. However high temperature of HVOF leads unexpected coating like a W_2C, Co_6W_6C or Co_3W_3C. These η-WC (W and W_2C) and decarburized coating are susceptible to corrosion and wear [4-6]. Comparing cold spray with high velocity oxy fuel (HVOF), one of thermal spray, cold spray coating layer contains only WC and Co [7].

One of other problem about WC is brittleness during coating. To improve deformability of WC, binder metal is added. For example, Co, Cr, Ni, Cu, Al, Fe or etc. [3]. Additionally, binder metal lowering melting temperature of composite powder increases coating properties. Among them, Co which is widely used as binder metal maintains mechanical properties like a hardness and improves corrosion properties [8]. However mechanical engineer needs to consider effect of radiation in nuclear power industry. Therefore Co is not suitable for binder metal of WC coating. In contrast, Ni has better corrosion resistance to alkaline environment and makes lower melting temperature. Moreover, in a view of cold spray, FCC structure has better deformability than BCC or HCP, and BCC has lowest deformability. WC is BCC structure so it needs binder metal. Ni makes better deformability than Co because Ni has FCC structure and Co has hcp structure [3].

In this experiment, we carried out WC-Ni cold spray coating by changing contents of Ni and observed coating quality for applying to secondary water chemistry environment as a proceeding research.

2. Experimental

2.1 Preparation

Carbon steel (90mm × 60mm × 5mm, POSCO) was used as substrate and its chemical composition is listed in Table 1. Prior to coating process, the surface was grit blasted and cleaned out by acetone solution in Rus Sonic Technology, Inc. (RSTI).

WC-Ni powder (15μm) is produced by agglomerated and spray dried method at Buffalo Tungsten Inc. (BTI). Weights of Ni in powder are 10% and 20% in composite WC-Ni powder. Raw materials of WC-Ni are nano size WC powder (300nm) and micro size Ni powder (2μm). And other Ni powder (15μm) is produced by electrolytic methods at RSTI. Chemical composition of powder is in Table 2. Powder image is in Fig 1.

After coating, carbon steel was cut to six small plate substrate (20mm × 20mm × 5mm) by electrical discharge machining.

Surface morphologies was investigated by scanning electron microscope (SEM). And energy-dispersive X-ray spectroscopy (EDS) was used to know chemical composition of surface.

2.2 Coating procedures

A low pressure cold spray machine (RSTI) was used for coating to carbon steel by using compressed air. We carried out WC-10Ni coating, WC-10Ni coating blending with different Ni powder composition. Finally WC-20Ni powder is coated to carbon steel substrate. Coating parameter is referred at preceded research and in Table 3 [9].

Table 1. Chemical composition of SA 516 Gr.60 (wt. %)

C	Si	Mn	P	S	Cu	Ni	Cr	Fe
0.13	0.201	0.714	0.0141	0.0041	0.006	0.01	0.006	Bal.

Table 2. Quantitative analysis on powder by EDS (wt. %)

	W	C	Ni	Fe
WC-10Ni	88.59	5.59	8.48	0
WC-20Ni	75.75	1.9	22.35	0
Ni	0	0.08	99	0.001

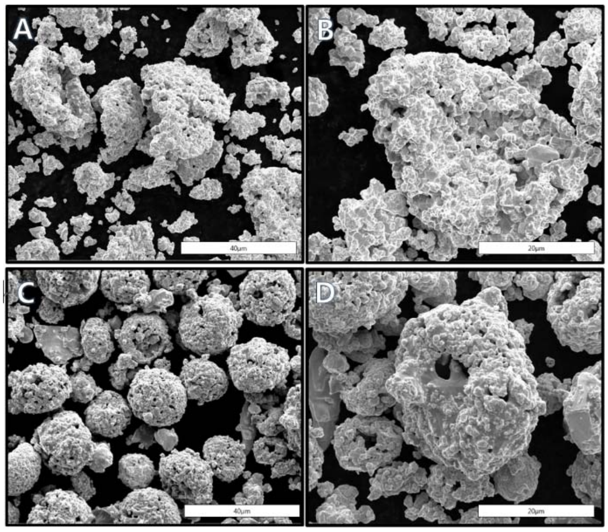

Figure. 1. SEM image of WC-10wt%Ni powder (A and B) and WC-20%Ni powder (C and D)

Table. 3. Coating parameter of cold spray

	Gas pressure (psi)	SOD (mm)	Temperature (°C)
WC-10Ni + 5%Ni	110	15	450
WC-10Ni + 10%Ni	110	15	450
WC-20%Ni	110	15	450

3. Results and Discussion

In Fig 1, WC-10Ni powder has characteristic which is hollow and broken form and fails to maintain spherical shape. In contrast, WC-20Ni maintains spherical and ball shape. It means Ni composition effects on powder shape and lower activation energy of composite powder due to form spherical shape. When Ni and WC powder is blended and agglomerated, blending of raw material powder is carried out sufficiently and temperature between WC and Ni melting temperature for making WC-Ni powder led agglomeration of Ni and WC located around Ni so other WC is agglomerated without Ni and seemed in SEM image, which is shown in Fig 1 (A).

Firstly, WC-10Ni powder was coated to substrates. Coating parameter was same in Table 3 and compressed air is used. However WC-10Ni was not coated to carbon steel surface and only eroded carbon steel. T. Schmidt's [10] powder in cold spray needs faster velocity than critical velocity that is minimum velocity for plastic deformation of powder during collision with surface. In equation (1) and (2),

$$\upsilon_{crit} = 667 - 0.014\rho + 0.08(T_m - T_R) + 10^{-7}\sigma_u - 0.7(T_i - T_R) \quad (1)$$

$$d_{crit} = 36 \cdot \frac{\lambda}{c_p \cdot \rho \cdot \upsilon_{particle}} \quad (2)$$

Table. 4. Nomenclature of equation

c_p	Specific heat
ρ	Density
υ	Velocity
λ	Thermal conductivity
T_m	Melting temperature
T_R	Reference temperature (293 K)
T_i	Impact temperature
d	Diameter
σ_u	Yield stress

melting temperature and particle diameter are main factor to critical velocity. Therefore high powder melting temperature and small particle raise critical velocity.

In WC-10Ni, 10%Ni less lower melting temperature than 20%Ni and smaller particle than 10μm in Fig 1 (A) led coating difficult. In cold spray condition on Table 3, the compressed gas made velocity between 550m/s to 590m/s. These velocity was insufficient compared to critical velocity, so increasing powder size is needed. Using N_2 or He gas as carrier gas is other method because these gas can increase velocity of power comparing compressed air.

However, additional Ni powder to WC-10Ni lowered critical velocity and made it possible to coat to carbon steel. Final coating was WC-20Ni. In Fig 1 (C) and (D), relatively large powder and high Ni contents of powder lowered critical velocity of powder and plastic deformation occurred.

Table. 5. Chemical analysis of coating (wt. %)

	W	C	Ni	O
WC-10Ni + 5Ni	78.84	02.57	17.49	01.10
WC-20Ni + 10Ni	65.93	02.99	23.76	07.32
WC-20Ni	75.32	02.43	20.71	01.54

Comparing A and C in Fig 2, increasing Ni contents of coating surface has an advantage for reducing porosity. Coating, using WC-10Ni, only was eroded at surface. However additional Ni powder made WC-10Ni to be coated before erosion and WC-Ni particle was attached to Ni powder in coated surface before end of plastic deformation of Ni powder. Difference of coating properties is explained in Fig. 3 by using schematic drawing. Because WC-10Ni powder having defected particle was used for WC-10Ni + 5Ni and WC-10Ni + 10Ni coating, it seemed that WC-20Ni coating has smoother surface than other coating. Table 3 means oxidation occurred in coating layer. It is expected oxygen penetrated in coating layer during electrical discharge machining. In Fig 2 (F), some particle having 5μm size and rock shape was observed. These particle is result of agglomeration of WC powder. In EDS data analysis, WC has 99% contents in these rock shape particle. The reason of these particle is powder production methods. In production process, small particle agglomerated at solution with high temperature and spray dried. Therefore WC nano particle agglomerated each other without Ni. And these defect will be disappeared by optimization of WC-Ni powder production methods.

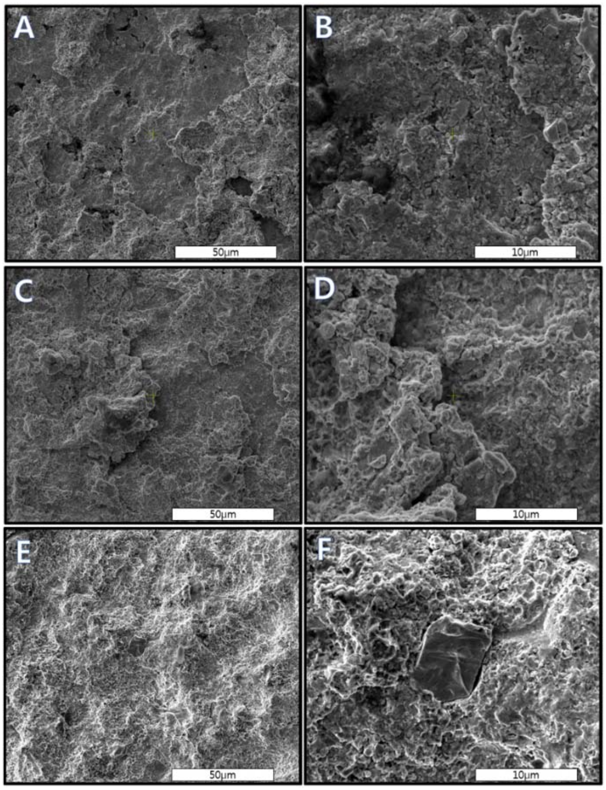

Figure. 2. SEM image of surface morphology of WC-10Ni + 5Ni coating (A and B), WC-10Ni + 10Ni coating (C and D) and WC-20Ni coating (E and F)

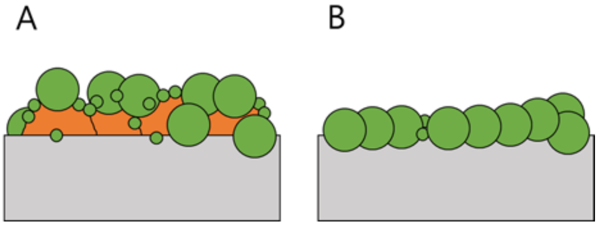

Figure. 3. Schematic drawing of WC-10Ni + Ni coating (A), WC-20Ni coating (B). Grey: carbon steel, Green: WC-Ni and Brown: Ni

4. Conclusions

High pH, high temperature and high pressure make flow-accelerated corrosion different from general corrosion. For mitigating FAC, coating experiments were carried out by using WC-Ni powder. Powder shape and coating quality of WC-10 + x%Ni and WC-20Ni are better than WC-10Ni because of different Ni composition. Therefore, coating quality for different Ni composition will have to be studied.

With optimizing powder production methods and coating parameter, corrosion experiments will be carried out.

5. Acknowledgement

This work was supported by the Nuclear Power Core Technology Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade Industry & Energy, Republic of Korea (No. 2013T100100029).

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