

ACCIDENT TOLERANT NUCLEAR FUELS AND CLADDING MATERIALS

# Development of Cold Spray Coatings for Accident-Tolerant Fuel Cladding in Light Water Reactors

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The cold spray coating process has been developed at the University of Wisconsin-Madison for the deposition of oxidation-resistant coatings on zirconium alloy light water reactor fuel cladding with the goal of improving accident tolerance during loss of coolant scenarios. Coatings of metallic (Cr), alloy (FeCrAl), and ceramic (Ti<sub>2</sub>AlC) materials were successfully deposited on zirconium alloy flats and cladding tube sections by optimizing the powder size, gas preheat temperature, pressure and composition, and other process parameters. The coatings were dense and exhibited excellent adhesion to the substrate. Evaluation of the samples after high-temperature oxidation tests at temperatures up to 1300°C showed that the cold spray coatings significantly mitigate oxidation kinetics because of the formation of thin passive oxide layers on the surface. The results of the study indicate that the cold spray coating process is a viable near-term option for developing accident-tolerant zirconium alloy fuel cladding.

## INTRODUCTION

The Fukushima-Daiichi accident in 2011 demonstrated the need for improved durability of zirconium-alloy claddings in light water reactors (LWR) during loss of coolant accident (LOCA) scenarios.<sup>1</sup> Under such high-temperature accident conditions, Zr alloys exhibit an exothermic oxidation reaction with water/steam that is accompanied by hydrogen gas release. The US Department of Energy's (DOE) industry-led Accident Tolerant Fuel (ATF) program is aimed at the development of alternative cladding and fuel concepts. Among the concepts being investigated is the deposition of coatings of oxidation-resistant materials on presently used Zr alloy claddings, which is deemed an attractive option for implementation in the near term. In this regard, a variety of coating materials and coating techniques have been investigated.<sup>2–6</sup> The University of Wisconsin, Madison (UW-Madison), under the auspices of the DOE's ATF program, has been collaborating with Westinghouse Electric Company (WEC) for over

3 years to develop low-temperature cold spray powder coating technology for the deposition of ceramic and metallic coatings on Zr alloy fuel claddings for improved oxidation resistance at elevated temperatures (> 1200°C). Based on initial successes, this concept has been selected for Phase 2 work of the ATF program aimed at in-reactor testing of lead test rods (LTR). In this article, development activities of a cold-sprayed Cr, FeCrAl alloy, and Ti<sub>2</sub>AlC coatings on Zr alloy flats and cladding sections at UW-Madison are introduced. The materials were chosen because of their inherent oxidation resistance derived from the formation of passive oxide scales such as Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>.<sup>7–10</sup> High-temperature ambient air exposures (e.g., 1300°C) of the coated Zr alloy tubes were performed to demonstrate the oxidation behavior of the coatings and their chemical interactions with the underlying Zr alloy substrate.

## EXPERIMENTAL

### Materials

All powders in this study were procured from commercial powder vendors. Two Cr powder types were investigated—electrolytically produced (99.8%

This article was updated to correct the title to read Light Water Reactors.

purity) and gas atomized (99.7% purity) powders. Fe-22.3% Cr-6.6% Al alloy powders containing 0.16 wt.% of yttrium (FeCrAl) were manufactured by gas atomization. Mo powders (99.8 wt.% purity) were manufactured by spheroidization process.  $\text{Ti}_2\text{AlC}$  powders were fabricated by mechanical attrition of a solid ceramic stoichiometric block produced by solid-state diffusion. Zr alloy cladding tubes provided by Westinghouse Electric Company (Hopkins SC, USA) were sectioned and surface polished in ethanol lubricant with 320 grit SiC abrasive paper before deposition.

### Cold Spray Process

In the cold spray process powder particles of the coating material are propelled at supersonic velocities onto the surface of a part (Zr alloy cladding tubes in this case) to form coatings with specific functionalities. The particle propulsion is achieved by pressurized and preheated inert gas that passes through a specially engineered nozzle (Fig. 1a). The particle temperature is low and deposition occurs in solid state, thus avoiding phase transformation and oxidation of the powder during deposition. Coating formation—both interparticle bonding and coating-substrate adhesion—occurs by plastic deformation and an associated adiabatic shear process.<sup>11</sup>

All cold spray work reported was performed at the University of Wisconsin, Madison. A commercial cold spray system (CGT Kinetiks 400/34 unit) and a six-axis industrial robotic system were utilized as shown in Fig. 1b. The pressure and temperature of working gases (pure  $\text{N}_2$  or  $\text{N}_2$ -He mixture) and other process parameters (powder feed rate, nozzle traverse speed, etc.) were optimized to achieve a high deposition rate, optimal coating thickness, and desired microstructure. In some cases the as-deposited coatings were polished to reduce surface roughness and thickness to yield a metallic surface appearance with roughness similar to that of the Zr alloy cladding tubes.

### Coating Evaluation and Characterization

The coated Zr alloy tubes were exposed to high temperature ambient air (e.g., 1000–1300°C) to assess their durability in oxidative environments. The coated

samples were introduced in a preheated furnace, maintained at temperature up to 20 min, and then air-cooled to room temperature. The high temperature exposure and the rapid heating and cooling also subjected the coatings to high thermal stresses and promoted chemical interaction between the coating and the substrate. Characterization of the powders and cross-sections of coated claddings were performed by a Zeiss LEO scanning electron microscope in conjunction with energy dispersive x-ray spectroscopy (SEM-EDS) and x-ray diffraction (XRD).

## RESULTS AND DISCUSSION

### Chromium Coatings

The as-received Cr powders were examined with SEM to confirm the size distribution and assess particle shape, both of which depend on the powder manufacturing process (Fig. 2). The electrolytically produced Cr powder had an irregular morphology consistent with mechanical attrition, while the atomized Cr powder, as expected, had a spherical morphology. The powders contained large particles in the 25–44  $\mu\text{m}$  range, which were sieved out to obtain an optimal particle size range for the cold spray process.

The Cr powders were deposited using pure nitrogen gas or a nitrogen and helium gas mixture for the propulsion gas—the lower molecular weight of helium provides increased velocity.<sup>12</sup> Cr coatings deposited using various parameter sets resulted in dense, continuous coatings on the Zr alloy, and the absence of delaminated regions at the coating-substrate interface in cross-sectional SEM images indicated good adhesion. The coatings produced by electrolytic and atomized Cr powders showed different microstructures. The Cr coatings deposited using atomized powder showed heavily deformed areas not evident in the coatings deposited using electrolytic powder. This is indicative of different deformation/bonding mechanisms during the cold spray process for the two types of Cr powders. Figure 3a and b shows high-magnification images of Cr cold spray coating microstructures produced with electrolytic and atomized powder using the same nitrogen and helium gas mixture. The microstructures of the coatings were indicative of dynamic recrystallization, which

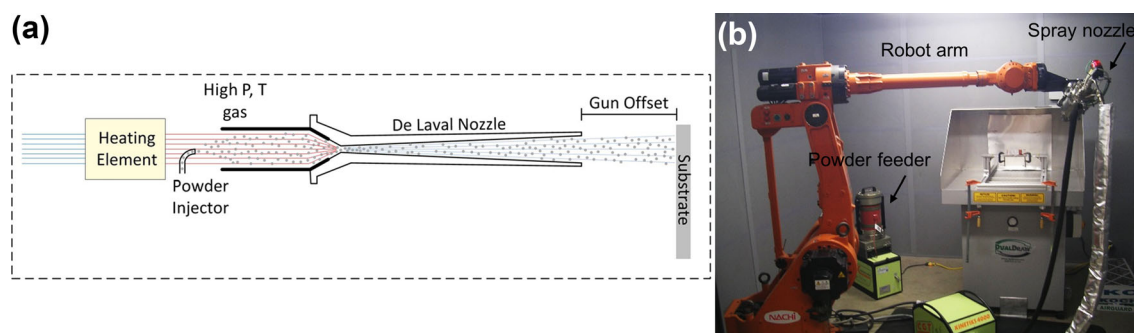


Fig. 1. (a) Schematic illustration of cold spray process and (b) photograph of the cold spray system at University of Wisconsin-Madison used in this study.

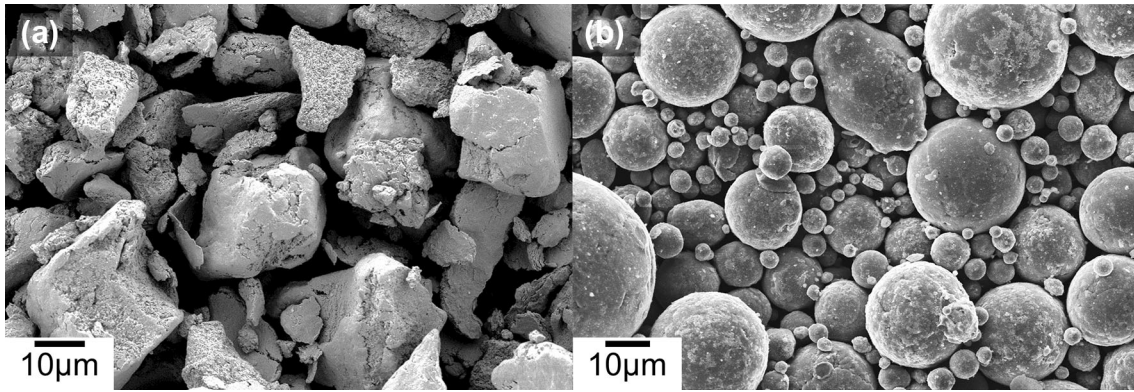


Fig. 2. SEM plain-view images of (a) as-received electrolytic Cr powder and (b) as-received gas atomized Cr powder.

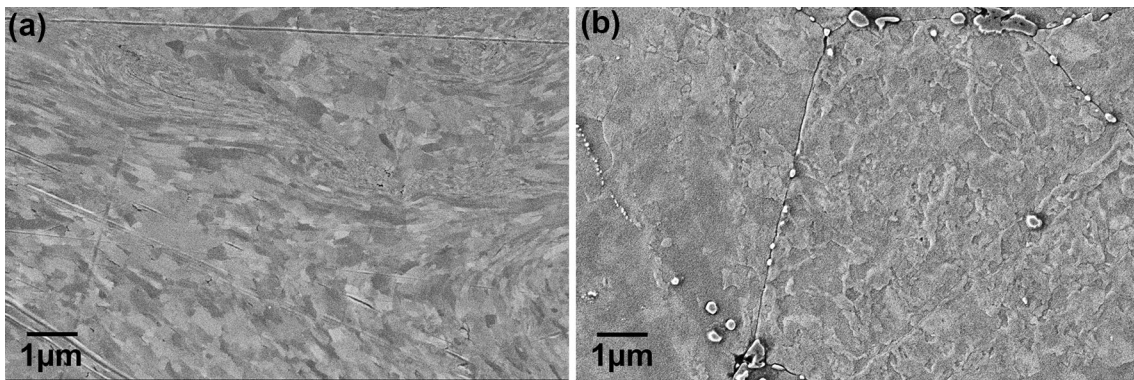


Fig. 3. SEM cross-sectional images of Cr coatings deposited using the same mixture of nitrogen and helium gases and either (a) electrolytic Cr powder or (b) atomized Cr powders. Etchant: Murakami reagent.

resulted in the formation of fine sub-micron-size grains, in addition to the heavily cold-worked areas. XRD analysis of the powders and the coatings (not shown here) showed identical patterns for the powders and the coatings, suggesting that no oxidation had occurred during the deposition process.

A section of the Cr-coated Zr alloy tube was exposed to ambient air at 1300°C for 20 min to investigate the high-temperature oxidation performance. The uncoated region on the inner diameter of the Zr alloy tube formed a ~150- $\mu\text{m}$ -thick Zr-oxide layer as shown in Fig. 4a, while the Cr coating formed a dramatically thinner (< 10  $\mu\text{m}$ ), dense, protective Cr-oxide layer (Fig. 4b). A thin < 5  $\mu\text{m}$  graded Cr-Zr inter-diffusion layer formed during exposure as evidenced by an EDS line scan shown in Fig. 4c. Further work to elucidate the Cr coating performance is on-going regarding the oxidation kinetics and inter-diffusion behavior during longer exposures.

### FeCrAl Coatings

Spherical FeCrAl alloy and Mo powders, produced by gas atomization and spheroidization, respectively, were obtained. Cold spray deposition was

performed on Zr alloy claddings using nitrogen propellant gas. Process parameters such as gas preheat temperature and gun translation speed were optimized to improve the microstructure, deposition rate, and coating-substrate adhesion. Details of the parametric investigation for the spray process are addressed elsewhere.<sup>13</sup> Although FeCrAl alloy coating has excellent oxidation resistance at elevated temperatures, rapid diffusion of Fe into the Zr alloy substrate with the associated low-melting-point eutectic formation (928°C for a binary Fe-Zr system<sup>14</sup>) renders direct deposition of FeCrAl on the Zr alloy ineffective. Therefore, a cold spray Mo coating was deposited as a diffusion barrier layer between the FeCrAl coating and Zr alloy substrate.

Figure 5 shows cross-sectional images after high-temperature exposure at 1200°C for 20 min in ambient air of the FeCrAl coating directly deposited on Zr alloy cladding and the FeCrAl coating on Zr alloy cladding with an intervening cold spray Mo diffusion barrier layer. For FeCrAl deposited directly on the Zr alloy, significant diffusion of the reactive elements (mainly Fe) into the Zr alloy substrate occurs with segregated microstructures

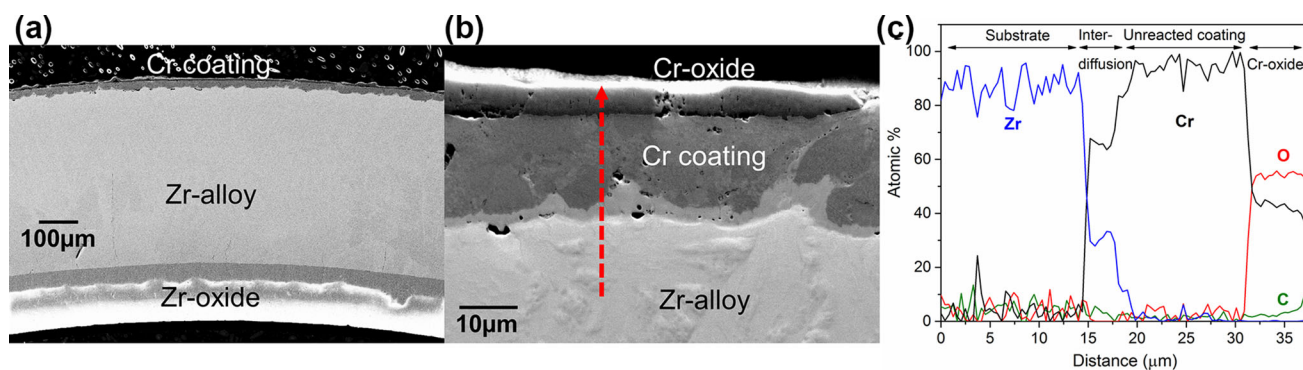


Fig. 4. Cross-sectional SEM images of the Cr-coated cladding section (atomized powder) oxidized at 1300°C for 20 min in ambient air: (a) a low-magnification image showing the dramatic decrease in oxidation on the coated versus the uncoated side, (b) a high magnification image of the Cr coating and thin oxide layer with the EDS line scan path (red dotted arrow), and (c) the resultant EDS line scan.

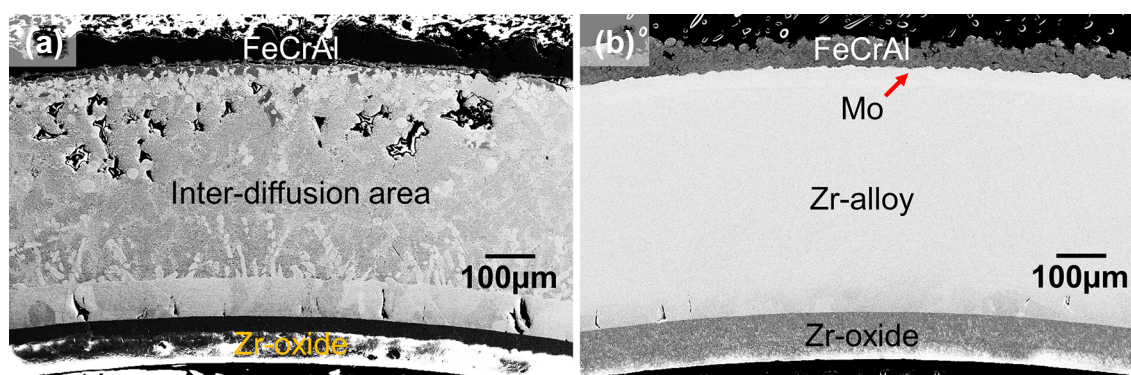


Fig. 5. Cross-sectional SEM images of samples after oxidation tests at 1200°C for 20 min in ambient air: (a) FeCrAl coating on Zr alloy cladding section; (b) FeCrAl coating on Zr alloy cladding section with a cold spray Mo diffusion barrier layer between the coating and substrate. The red arrow indicates the thin Mo layer.

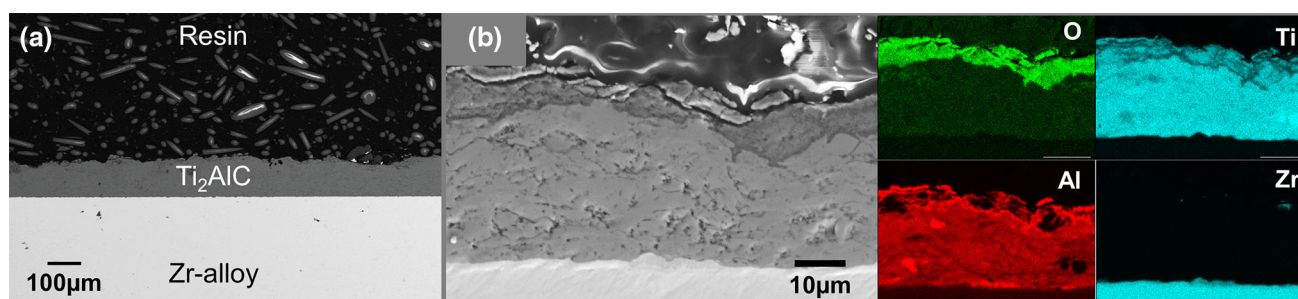


Fig. 6. SEM cross-sectional images of (a) as-deposited  $Ti_2AlC$  coating on Zr-alloy and (b)  $Ti_2AlC$  coating after 1000°C, 7 min air oxidation with corresponding EDS elemental maps that suggest preferential alumina formation on the oxidized coating surface.

typical of eutectic melting and solidification. However, the Mo barrier coating successfully mitigated the detrimental inter-diffusion between FeCrAl and the Zr alloy. In both cases, the thin passive alumina layer on the top of the FeCrAl coating was highly protective and prevented oxygen ingress from the environment into the Zr alloy substrate. The uncoated inner surface of the Zr alloy tube showed an approximately 100- $\mu$ m-thick oxide layer.

### $Ti_2AlC$ (MAX-Phase) Coatings

As-received  $Ti_2AlC$  powders (< 20  $\mu$ m size) were deposited on the Zr alloy using nitrogen propellant gas. The details of the powder morphology and spray process are addressed by the present authors in a previous publication.<sup>2</sup> A SEM cross-sectional image of the  $Ti_2AlC$  coating on the Zr alloy substrate in Fig. 6a shows the coating to be about 100  $\mu$ m thick and free of cracks and pores. It is noteworthy that the cold spray process, which

typically relies on particle plastic deformation, produced a reasonably thick  $Ti_2AlC$  ceramic coating on the metal substrate. It is speculated that the underlying particle-bonding mechanisms are dramatically different from the Cr and FeCrAl metallic coatings, and further work is underway at the University of Wisconsin to understand the mechanism of bonding for these powders. Figure 6b shows an SEM cross-sectional micrograph of the coated Zr alloy with corresponding EDS elemental maps after an initial oxidation study at  $1000^\circ C$  for 7 min in ambient air. The  $Ti_2AlC$  coating formed a  $10\text{-}\mu m$ -thick oxide scale with no oxidation of the Zr alloy at the coating substrate interface. The uncoated sample showed a  $25\text{-}\mu m$ -thick zirconium oxide. The oxide scale on the  $Ti_2AlC$  coating consisted of a mixture of titanium and aluminum oxides based on the EDS analysis. Additionally, the enhanced wear resistance and high hardness values of these coatings have been previously reported by the present authors.<sup>2</sup>

### CONCLUSION

Example results of the on-going research program to develop cold spray-coated ATF claddings in a collaborative program between the University of Wisconsin, Madison, and Westinghouse Electric Company have been reported. Cr coatings with two powder types, FeCrAl coating with an Mo interlayer and  $Ti_2AlC$  ceramic coatings, were successfully deposited on Zr alloy cladding tube sections with the goal of enhancing high-temperature oxidation resistance. Cold spray parameters such as the gas preheat temperature, pressure, and composition and gun traverse speed were optimized to achieve the desired deposition rate, coating microstructure, and coating-substrate adhesion. Exposure of the coating-substrate system to high temperatures ( $1000^\circ C$  or higher) showed the coatings clearly provided enhanced oxidation resistance

compared to the Zr-alloy substrate, demonstrating their potential for the development of ATF cladding. In fact, the cold spray-coated claddings reported in this article are being or have been subjected to in-reactor testing and other prototypical mechanical and thermal tests to simulate in-reactor conditions.

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