

YEAR-END SUMMARY REPORT

TITLE: Deposition Routes for the Development of Multi-Functional Coatings for Naval Application via Nano-Engineering Methods

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BACKGROUND:

Formation of amorphous microstructures by quenching from the liquid phase generally requires thermal spray cooling rates on the order of 10^4 - 10^6 K/s during rapid solidification.¹⁻⁵ As noted in the literature, recent advances in the production of bulk metallic glasses have reduced this rate by orders of magnitude. Several alloy systems have formed amorphous structures at extremely slow cooling rates: $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ (10^2 K/s),³ $\text{Ni}_{62}\text{Nb}_{38}$ (10^3 K/s),³ $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ (10^2 K/s),⁶ and a Zr-Ti-Be alloy (1 K/s).⁷ Thermal spray technology combines the processes of very high temperature melting, quenching, and consolidation into a single operation, offering an excellent opportunity to produce amorphous or nano-crystalline coatings. Thermal spray techniques such as atmospheric plasma and HVOF have solidification rates of 10^6 - 10^8 K/s⁸⁻¹² and 10^7 K/s,^{13,14} respectively, and are likely candidate processes for amorphous and nano-crystalline/amorphous formation. Several amorphous, nano-crystalline, or quasicrystalline alloy coatings have been produced by atmospheric plasma spraying¹⁵⁻²⁰ as well as by HVOF spraying^{3,21-28} and flame spray.²⁶ It should be noted that although plasma spraying offers a high quench rate, annealing of the thermal spray deposit occurs as a result of both the high temperature plasma flame and adiabatic recalescence associated with particle solidification of one splat droplet upon another. This annealing can lead to degrees of devitrification of the sprayed metallic glass.^{9,15}

OBJECTIVE: The goal of this metallic coatings effort was to create a reproducible, easily-applied, metallic coating that replaced the hot-roll bonded cladding systems currently used on military aircraft. This coating requires a range of functions to improve corrosion performance, coating adhesion, and provide active corrosion protection. The implementation of thermal spray technology provides optimal coating and substrate properties and the use of nano-crystalline or amorphous matrix metallic with desired alloying elements produces a material with superior corrosion performance, high strength, ductility, and wear resistance. Further, the ability to utilize alloy compositions that contain rare-earth elements make it possible to produce a cladding material with active corrosion protection properties at coating defects or mechanical scratches. Appropriate glass forming chemistries were determined and produced in ingot/powder form and deposited as nano-crystalline coatings. Hardness and fatigue testing indicated that the first coatings sprayed were brittle with degraded fatigue life. Because the mechanical properties, especially fatigue properties, are essential for the use of this coating in aircraft applications, the processing was optimized to satisfy the requirements for mechanical and corrosion properties.

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METHOD AND RESULTS:

Initial experimentation on the application of amorphous cladding onto AA2024-T3 employed pure aluminum and demonstrated that a coated material with improved corrosion and fatigue properties was achievable. A 99.0-99.8 % Al coating/AA2024-T3 skin substrate system was used to evaluate the corrosion/fatigue performance as a function of thermal spray coating process (i.e., powder flame spray, atmospheric plasma spray, and HVOF spray, and cold spray processes). Comparison of the microstructures, mechanical properties, fatigue, and pre-corroded fatigue properties of samples with the three types of thermal spray coating, as well as samples of bare AA2024-T3 and Alclad™ AA2024-T3, revealed that HVOF was the most promising thermal spray process of those evaluated for the deposition of aluminum coatings. In particular, HVOF coatings greatly increase the fatigue and pre-corroded fatigue lifetimes of the AA2024-T3 substrate. The HVOF process, however, did not seem to significantly reduce the grain size of the feedstock powders and therefore, to produce an amorphous or nano-crystalline coating, an amorphous or nano-crystalline feedstock may need to be obtained. A possible alternative deposition method for production of nano-crystalline coatings is pulsed thermal spray or cold spray.

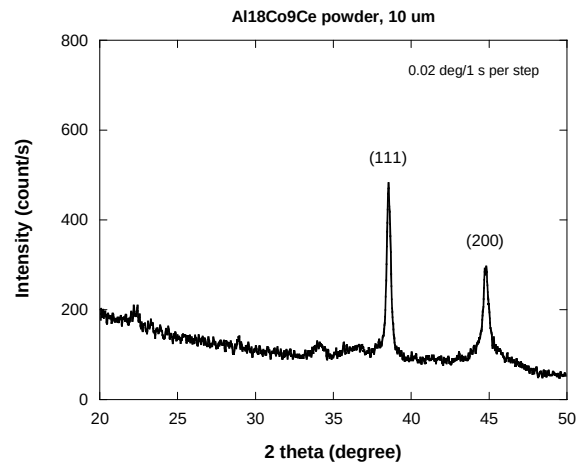
Prior to selection of the optimal chemistry, 40 µm size powders of a possible glass-forming composition (Al-6Co-5Ce by weight) were purchased from AlPoCo in the United Kingdom and were evaluated. Some powders were also provided to SAIC, developers of the HVOF Pulsed Thermal Spray (PTS) process, a variation of thermal spraying that involves melting and rapid solidification, and thus reduces grain size. Slow scan rate x-ray diffraction indicated lower peak intensities and some peak broadening for the PTS coating, demonstrating that the pulsed process can refine the grain structure of the starting feedstock. Additional Al-18Co-9Ce (by weight) powders with a finer powder size (approximately 10 µm) were purchased for the PTS method since research has indicated a finer feedstock may yield an even finer coating grain size. Feedstock powders and processed coatings deposited were characterized by x-ray diffraction and Scanning Electron Microscopy (SEM) to identify the structure. X-ray diffraction patterns, as shown in Figure 1 indicated that feedstock powders and processed coatings were nano-crystalline in structure. The composition analysis by EDS showed that the microstructure of the Al-18Co-9Ce PTS coating consisted of Al-16Co-10Ce matrix, Al-54.4Co-3.2Ce-3.40 and Al-26.8Ce-32.10 inclusions or constituents (by weight). A fine dendrite grain structure on the order of 85 nm in size was evident in areas of the coating matrix. X-ray mapping revealed that the PTS coating was relatively uniform with small amount of oxygen uptake. These results indicate that Al-18Co-9Ce system is more glass-forming and PTS coating process is able to refine the grain size of the starting powder. The main advantage of the PTS technique is the ability to deposit an amorphous or nano-crystalline coating using traditional crystalline feedstock.

The optimal glass forming chemistries were determined by Scully and Shiflet to be Al-13Co-26Ce (by weight). Ingot materials were purchased from Arris International and atomized into amorphous/nano-crystalline feedstock powders at Valimet. SEM images indicated that Al-13Co-26Ce feedstock powders were about 10 µm in particle size and processed coatings produced via modified cold spray, as shown in Figure 2, were dense. Coatings produced via PTS using the 10µm powders were varied with varying process parameters. A table of porosity and oxide

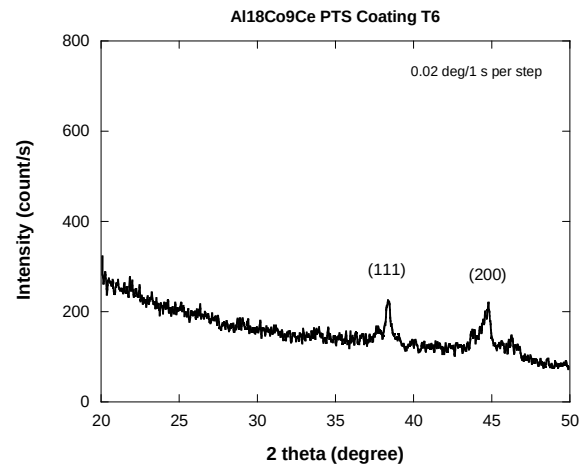
measurements, demonstrating the range of both which can be obtained by varying the process, for one batch of samples is given in Table 1. Representative micrographs and diffraction patterns for a coating with low porosity and oxide versus one with higher values are given in Figure 3. PTS coatings tend to demonstrate a higher degree of amorphousness, as shown in the x-ray diffraction pattern given in 3(d) as compared to the one in 3(b) where the coating has higher amounts of porosity and oxides present.

Attempts were made by two thermal spray sources to deposit the 10 μ m powders using HVOF methods but powder feed issues, due to the fineness of the powder, could not be overcome. Coarser Al-13Co-26Ce feedstock powders were used since the diffraction pattern for the 45 μ m shown in Figure 4 indicates similar nano-crystallinity to the 10 μ m powders for the same composition. Powders were forwarded to CDNSWC and F.W. Gartner Thermal Spraying, Ltd for HVOF coating deposition. Representative coatings and x-ray diffraction patterns are shown in Figure 5. The Gartner coating appears more uniform and more amorphous and can be modified to produce any even more amorphous product as shown in Figure 6. Hardness and fatigue testing indicated that the first Al-13Co-26Ce (wt%) HVOF coatings sprayed were brittle with degraded fatigue life. A subsequent investigation brought to light the variations in sample preparation as compared to past methods, which has been corrected. Because the mechanical properties, especially fatigue properties, are essential for the use of this coating in aircraft applications, processing conditions as well as substrate preparation must be optimized or the composition altered to satisfy the requirements for mechanical and corrosion properties.

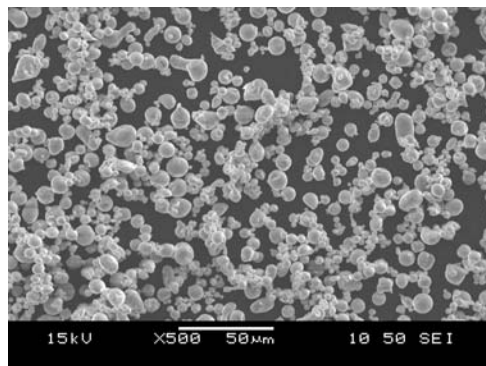
An evaluation of available, commercially developed cold spray methods such as Kinetic Metallization was also conducted. The resulting coating demonstrated the high strength and reduced ductility associated with cold working so that fatigue properties were limited. Alternative cold spray techniques, in particular the method recently developed at University of Ottawa and shown in Figure 7a, have been pursued. Preliminary fatigue results for cold spray coatings are very promising as shown in Figure 7b. Additional chemistries have been produced in ingot form and atomized into powders having a range of sizes.



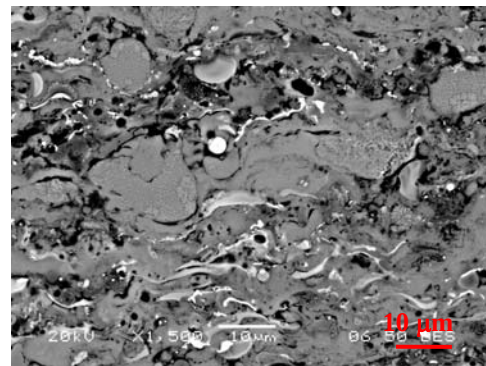
(a)



(b)



(c)



(d)

Figure 1. X-ray diffraction patterns and SEM images of Al-18Co-9Ce feedstock powders and HVOF PTS coating.

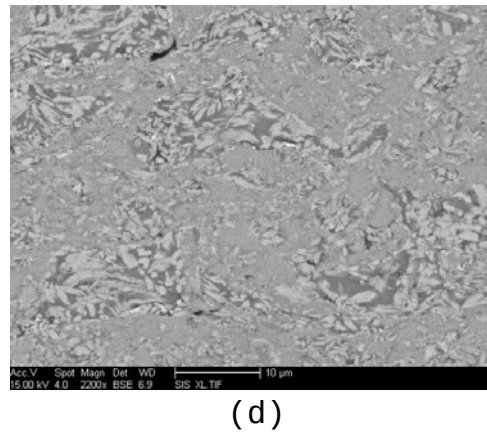
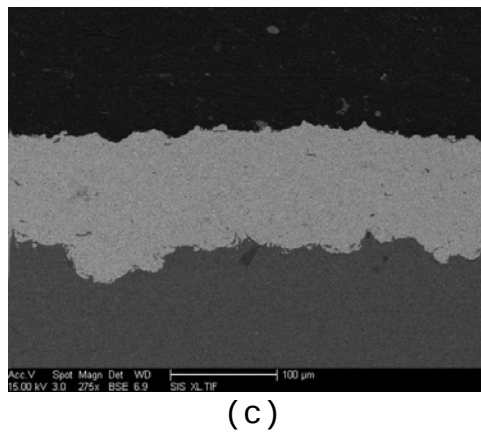
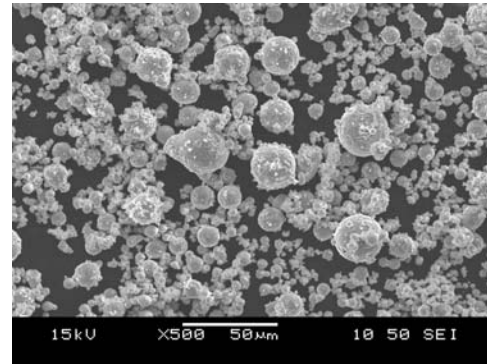
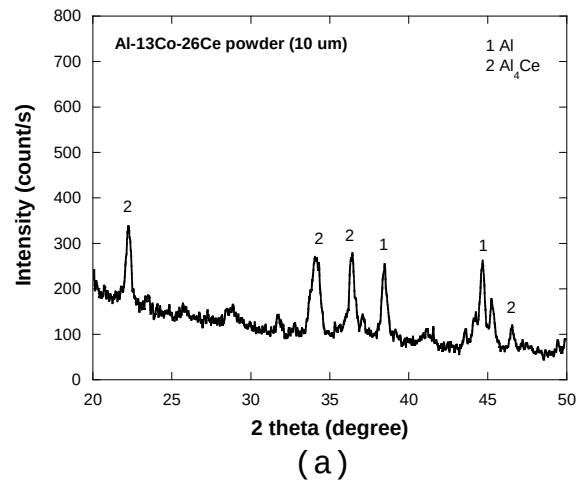
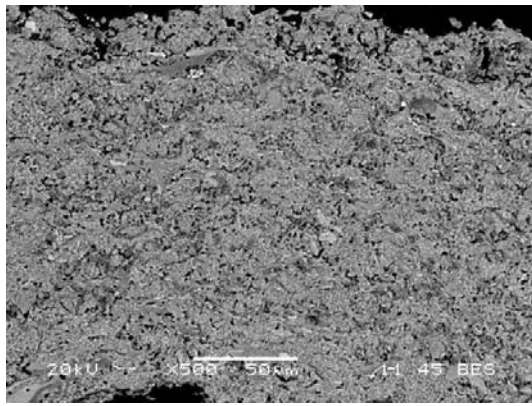
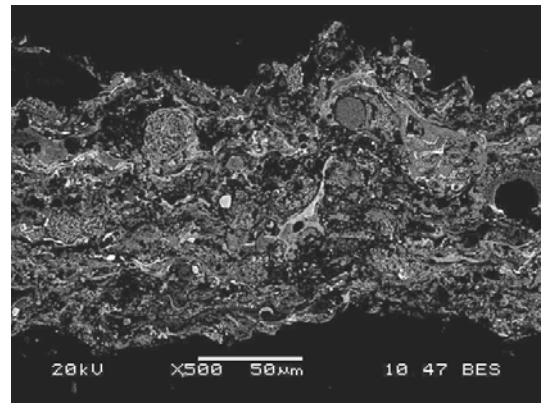


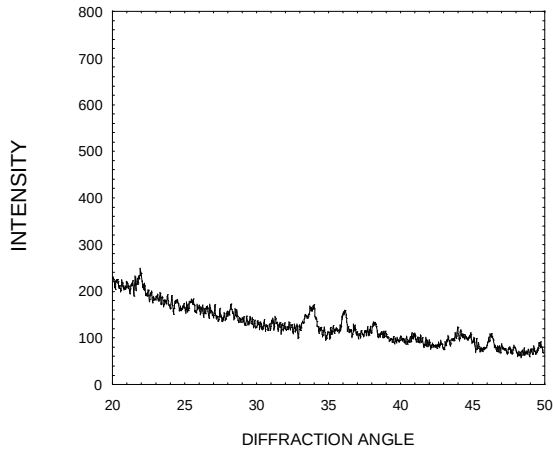
Figure 2. X-ray diffraction pattern and SEM images of Al-13Co-26Ce feedstock powders and cold spray coatings.



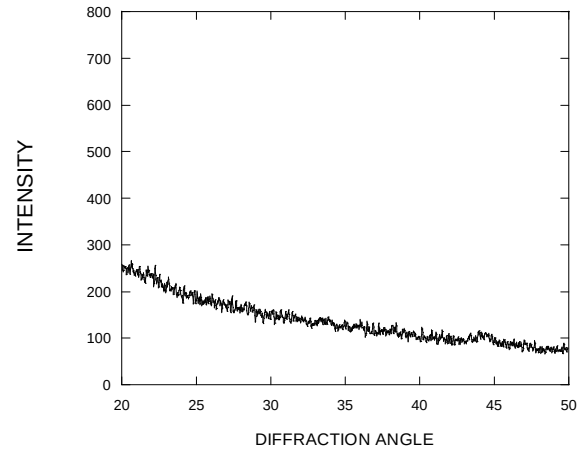
(a)



(b)



(c)



(d)

Figure 3. SEM images and x-ray diffraction patterns for PTS coatings deposited using Al-13Co-26Ce feedstock powders. Low porosity and oxide values were determined for the coating shown in (a) with its XRD pattern in (c) and high values were determined for the coating shown in (b) and (d).

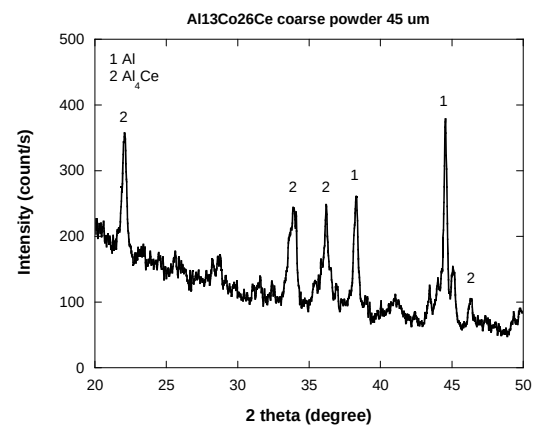
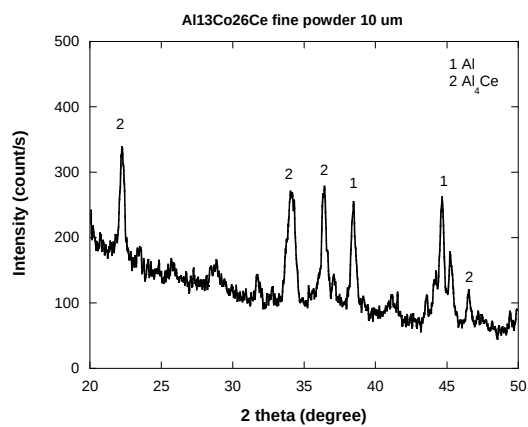
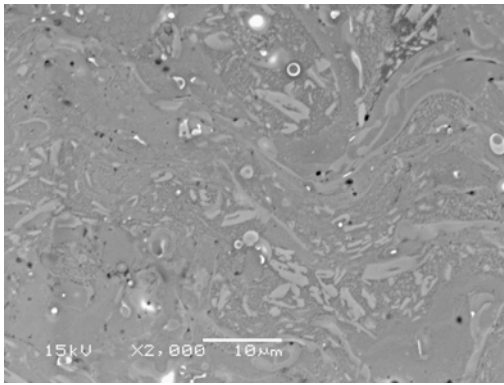
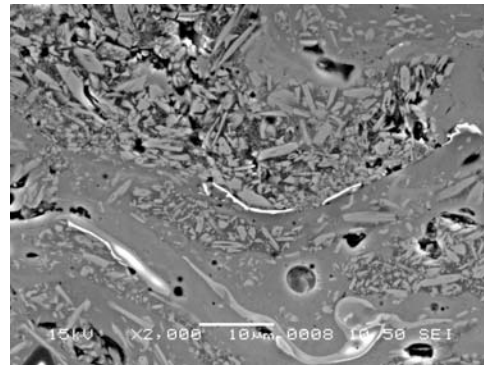


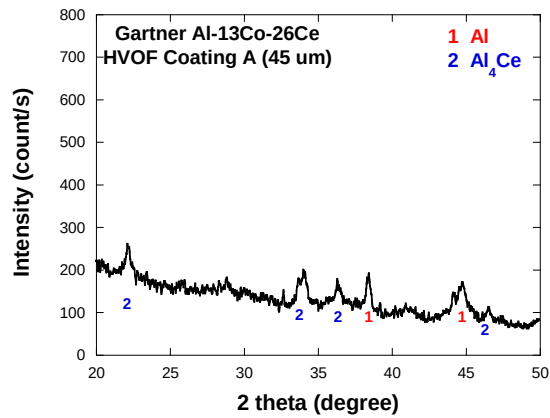
Figure 4. X-ray diffraction patterns for Al-13Co-26Ce feedstock powders.



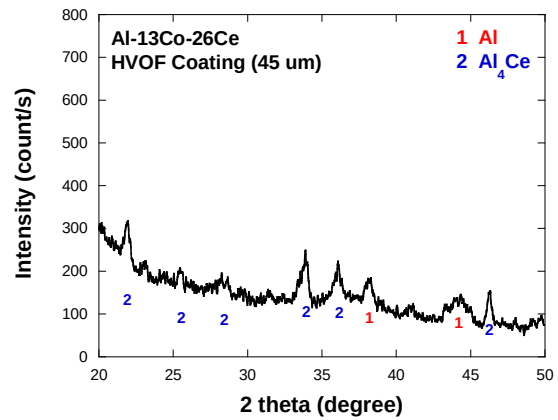
(a)



(b)



(c)



(d)

Figure 5. Representative coatings and x-ray diffraction patterns for HVOF coatings produced at F.W.Gartner (and c) and CDNSWC (b and d).

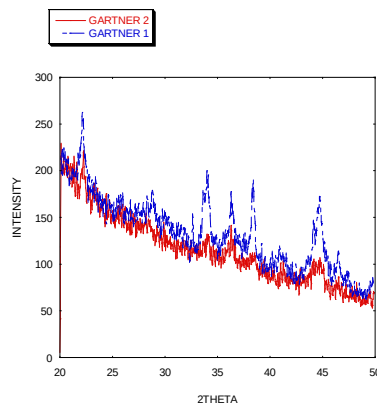


Figure 6. Subsequent Gartner coatings represented by the pattern in red have shown reduced crystalline peaks as compared to earlier coatings, represented by the blue.

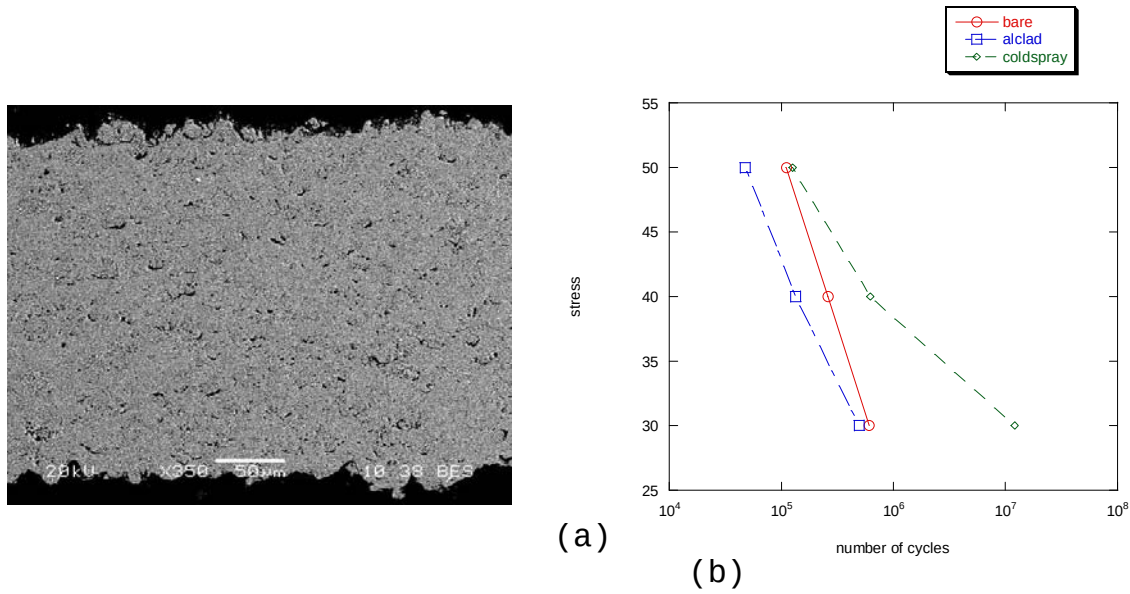


Figure 7. SEM images of Al-13Co-26Ce coatings (a) and coating fatigue properties as compared to bare AA2024 and Alclad (b).

TABLE 1. Quantitative Analysis of PTS Al-13Co-26Ce Coatings

	Microhardness Vickers 300g Average of 5 measurements	Oxygen Wt% (SEM) Average of 3 measurements	Porosity % (Optical Microscopy)	Oxide % (Optical Microscopy)	Number of samplings for porosity and oxide%
A1A	197.9	5.5	1.38	4.15	Ave of 7
A2	168.2	6.3	0.662	4.24	Ave of 4
A3	164.3	6.6	3.06	7.22	Ave of 2
A4	166.1	6.1	0.745	4.15	Ave of 7
A5	168.9	7.2	1.93	8.2	Ave of 4
A6	214.8	7.5	1.29	6.09	Ave of 7
A7	212.1	12.1	6.77	26.71	Ave of 5
A8	203.5	8.0	2.00	17.67	Ave of 3

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PUBLICATIONS:

"The Transformation of an Al-based Crystalline Electrode Material to an Amorphous Deposit via the ElectroSpark Welding Process"

S. Cadney, G. Goodall, G. Kim, A. Moran, M. Brochu, published in Journal of Alloys and Compounds 476 (2009) p147-151

PRESENTATIONS:

"Mechanical Characteristics of Al-Co-Ce Coatings Produced by the Cold Spray Process" E. Sansoucy, B. Jodoin, G. E. Kim, A. L. Moran, International Thermal Spray Conference Proceedings, Beijing China, May 2007.

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Date

Signature