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Analysis of Ta/Ni Multilayer Cold Spray Coatings

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ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
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Analysis of Ta/Ni Multilayer Cold Spray Coatings

Christopher P. Mulligan and Allison M. Welty

Abstract

Characterization was completed on two multi-layered cold spray coatings. The samples consisted of flat steel substrates coated with ~820 µm of Ni and a topcoat of ~210 µm Ta deposited via cold spray. Characterization was completed to determine thickness, structure, and adhesion of the coatings. To determine coating thickness and structure metallographic analysis was completed. Adhesion was analyzed via groove adhesion testing. Further analysis to determine constituents of cold spray coatings was completed via SEM-EDS.

Keywords

Coatings, Cold spraying, Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Tantalum, Nickel

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INTRODUCTION

This report describes the characterization of metallic coatings using the cold spray process (also referred to as kinetic spray)[1,2]. The coating process involves accelerating metallic particles to high velocities through a nozzle via the kinetic energy of a compressed gas. The metallic particles impinge on a substrate surface to generate coatings. The cold spray process is a high rate deposition process comparable to thermal spray processes but completed at much lower temperatures (Ono bulk particle melting, oxidation, solidification stresses, etc.).

COLD SPRAY DEPOSITIONS

Two tantalum over nickel multilayer cold spray deposited samples were provided by Army Research Laboratory for analysis. The samples were deposited on flat steel coupons with dimensions of 1.56” x 0.75” x 0.375”. One sample was sectioned and characterized, while the second was archived for possible vented erosion simulator (VES) test firing. The precise cold spray parameters of particle size, temperature, and particle velocity are unknown for the Ni and Ta layers. The following characterization tests were performed on the specimen designated:

- Sectioning and visual inspection
- Coating thickness
- Metallographic analysis and microhardness
- Groove adhesion testing
- Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM-EDS) surface analysis

SECTIONING AND VISUAL INSPECTION

Both cold spray samples were comprised of a Ni bond coat and a Ta top coat. The sample identified as CS2005-126-3 was archived for possible VES testing, while the sample CS2005-126-4 (CS-4) was chosen for characterization. Both samples appeared to have a smooth, ground finish, indicating a machining procedure following the cold spray process.

Characterization specimens were cut from sample CS-4 for metallography and groove adhesion testing. For metallographic analysis both a transverse and longitudinal cross-section were taken. No signs of coating spallation or fracture were observed during sectioning.

COATING THICKNESS

Ta coating thickness was uniform across the small sample at 210±15 µm. The Ni bond coat thickness was also uniform but much thicker at 820±20 µm as indicated in Figure 1.

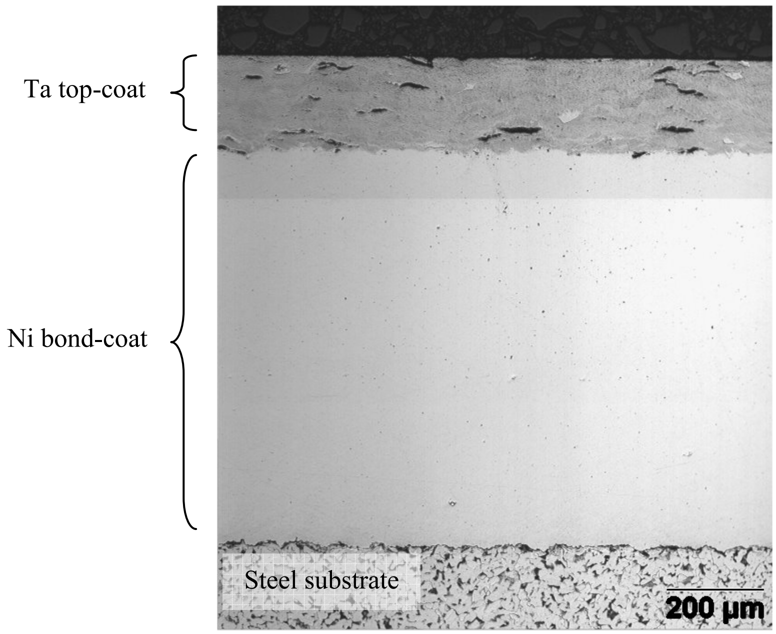

Figure 1. Cross-section of ARL cold spray specimen illustrating thickness variation.

METALLOGRAPHIC ANALYSIS AND MICROHARDNESS

The steel microstructure is indicative of a hypoeutectoid steel that has been heated into the austenitic range and slow cooled. The resultant microstructure is a mixture of proeutectoid ferrite (light phase) and pearlite (dark phase) as illustrated in Figure 2. Knoop microhardness indents give an average microhardness of HK_{50} 265 vs. HK_{50} 425 – 450 for a typical tempered martensitic gun steel. This softer material may help to enhance the bond between coating and substrate.

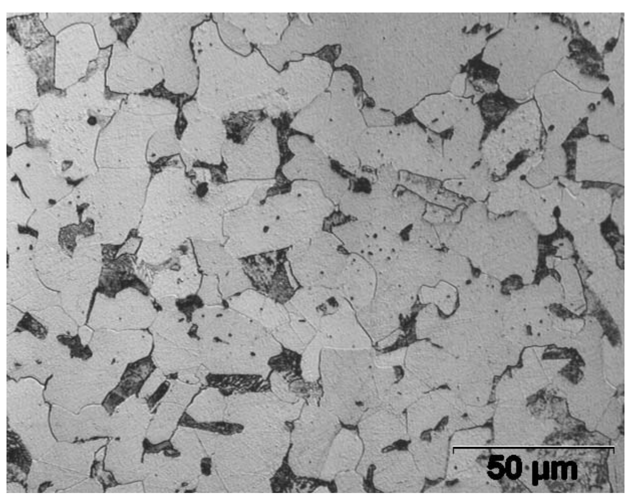

Figure 2. Microstructure of steel after etching.
The light constituent is ferrite; the dark constituent is pearlite.

The Ni bond-coat is dense as illustrated in Figure 3. The cold spray technique leads to a scalloped work-hardened structure as illustrated in the inset image. The microhardness of the Ni is substantially harder than the underlying substrate at ~HK_{50} 450-500.

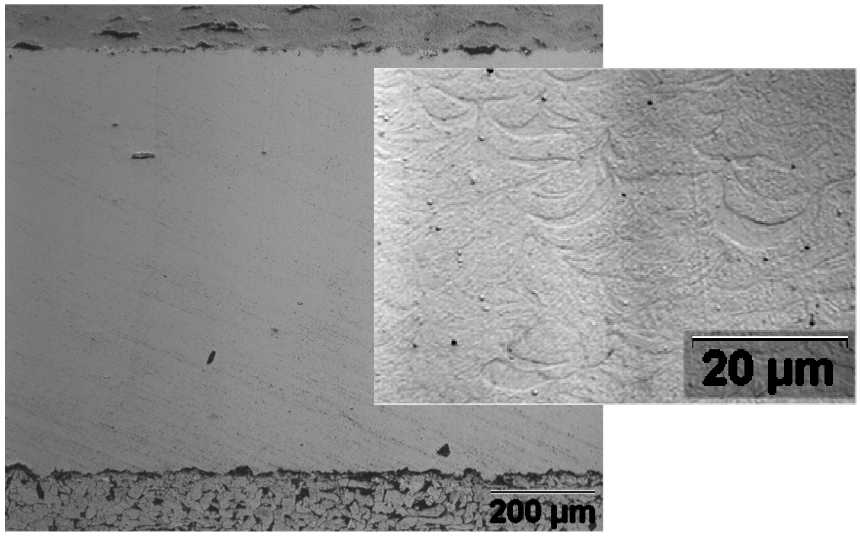

Figure 3. Cross-section of Ni bond-coat and at high magnification (inset).

The interface between the Ni bond-coat and the steel substrate is illustrated in Figure 4. The impact of the high velocity Ni particles results in severe plastic deformation of the soft steel as illustrated by the image inset. The structure of the interface is similar to that of a friction or explosive weld. The dense, irregular interface in the absence of porosity as shown here should result in excellent adhesion of the Ni to the substrate. The bombardment of Ni particles and the subsequent "stirring" of the steel should also assist in breaking up any oxides that might otherwise hinder adhesion. One issue that must be considered is whether this level of deformation would occur on a harder martensitic gun steel structure. It is difficult to predict what the morphology of the interface would be in this case.

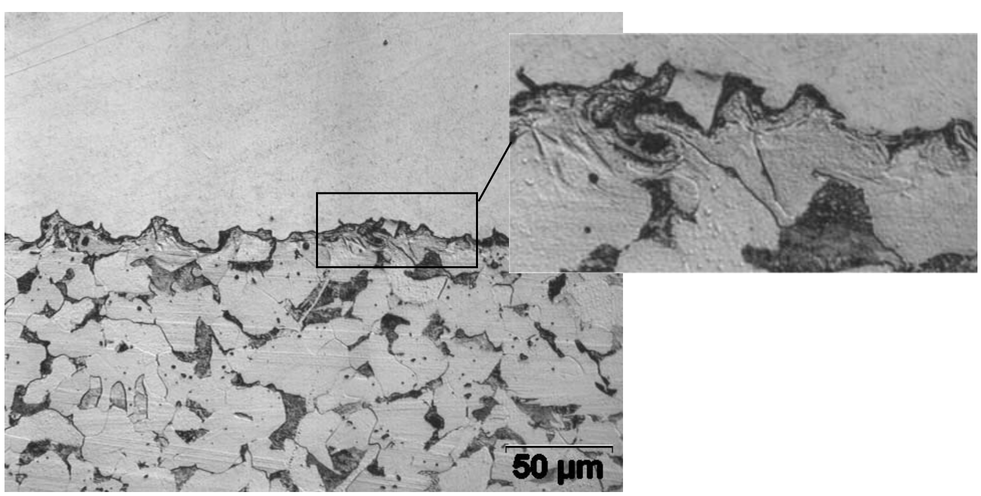

Figure 4. Interface of Ni bond-coat and steel substrate in cross-section.

The structure of the Ta top-coat is less dense than the Ni bond-coat as illustrated in Figure 5. There is substantial variation in the porosity, which tends to run normal to the impingement direction of the Ta particles. The increased porosity is most likely due to two factors. Those being, Ta is substantially denser than Ni (16.65 g/cm^3 vs. 8.91 g/cm^3) and has a much higher melting point (2996˚C vs. 1455˚C). The orientation of the porosity is of concern as it may result in lamellar failure where large portions of the coating may spall during a wear event. Additionally, in many areas, there is porosity directly along the interface of the Ta and Ni. This may result in premature adhesive failure.

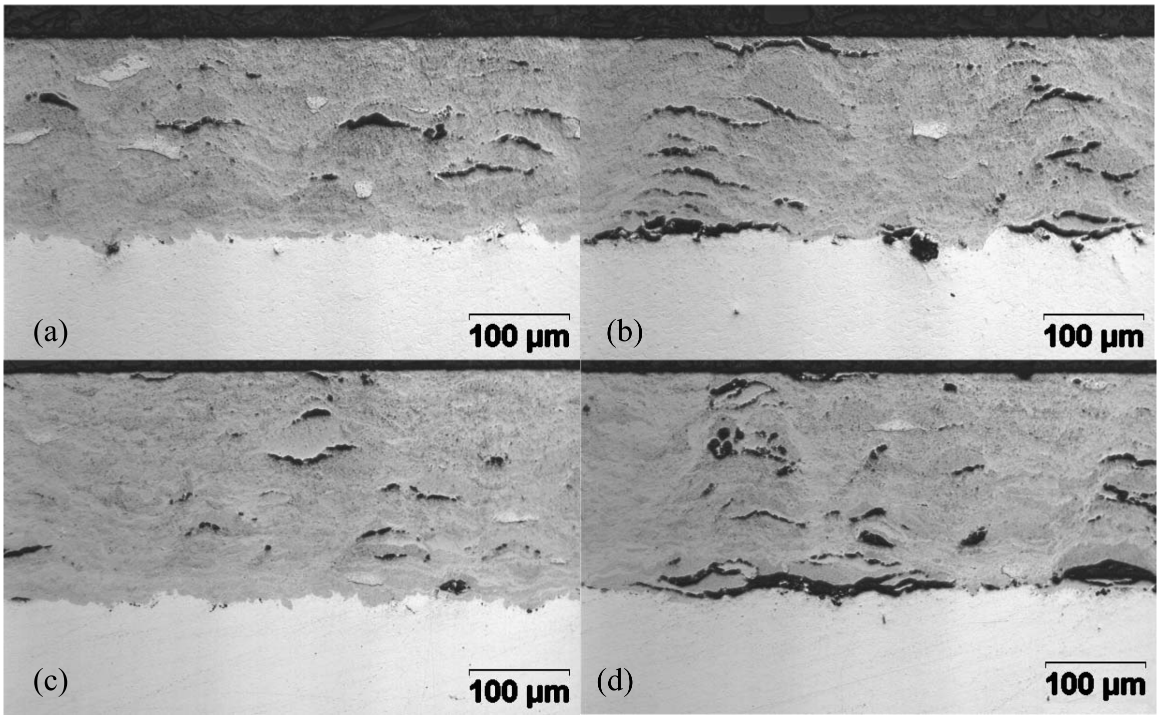

Figure 5. Metallographic images in cross section of the Ta top-coat showing varying degrees of porosity. Images (a) and (b) are longitudinal cross-sections, while (c) and (d) are transverse.

Figure 6 illustrates the Ta-Ni interface at high magnification. As illustrated in Figure 6 (a), where porosity is not present the interface exhibits good intermixing of the Ta and Ni. Figure 6 (b) illustrates the porosity that can occur and in this case some foreign debris that may have impeded bonding.

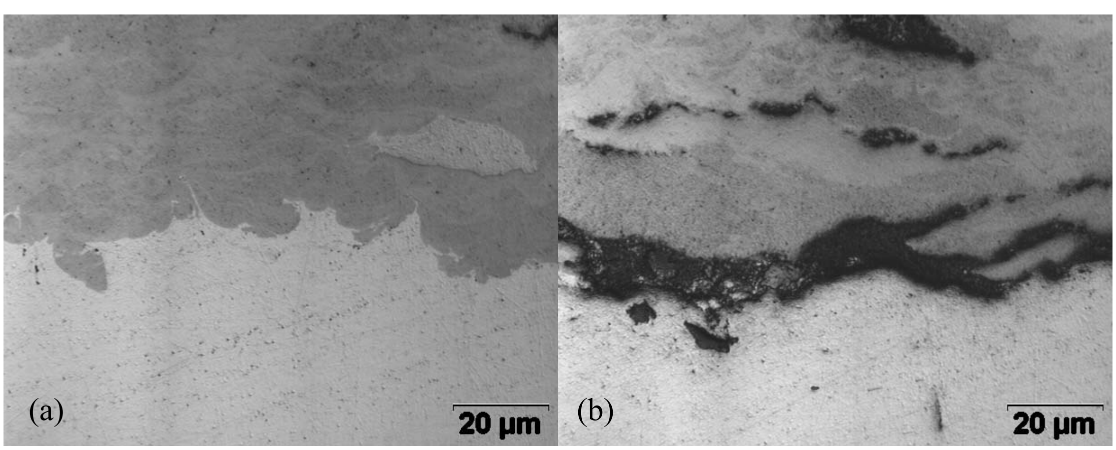

Figure 6. Interface of Ta top-coat and Ni bond-coat in cross-section.
(a) dense interface (b) porous interface.

The structure of the Ta top-coat is not homogenous and has some distinct texturing. Differences in reflectivity as illustrated in Figure 7 often indicate differences in structure, hardness, and/or density/morphology. In this case the slight differences in reflectivity appear to be changes in density with the slightly darker areas being more porous. The hardness of the coating ranges widely from HK_{50} 400 – 600 between these regions.

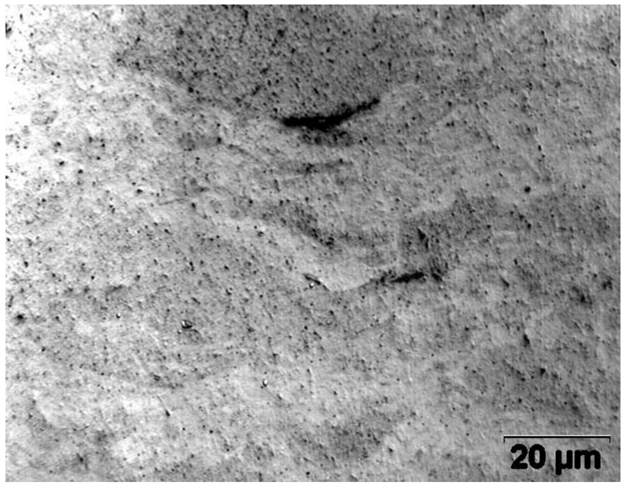

Figure 7. Cross-section of Ta top-coat showing differences in reflectivity that appear to relate to density/ morphology.

Also present are numerous inclusions which are not hard enough to be intermetallics or metastable phases of tantalum. The hardness of these inclusions was measured to be ~HK_{10} 500 – 550. This is very close to the hardness of the Ni bond-coat and the inclusions have the same reflectivity as illustrated in Figure 8. It is unclear as to how the Ni became embedded in the Ta top-coat. A possible explanation is the powder feed mechanism had a substantial amount of Ni powder still present when Ta deposition began.

Overall, the average hardness is much higher than bulk (HK_{50} 100-130) or even work-hardened Ta (HK_{50} 200-300). This may be due to incorporation of impurities during cold-spray and/or an alloying effect of the Ni in the Ta.

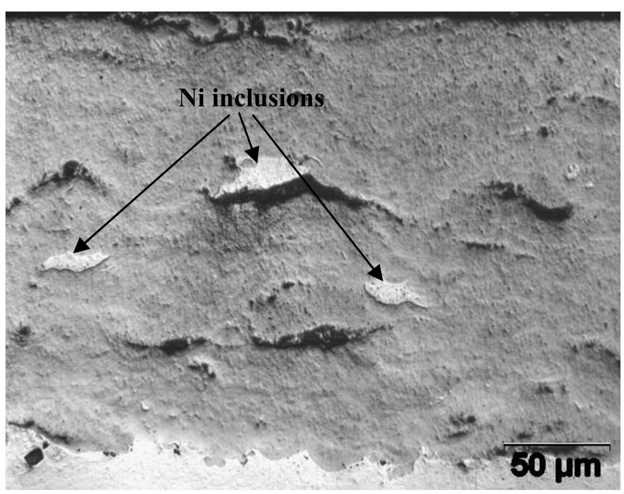

Figure 8. Cross-section of Ta top-coat.
The light colored inclusions appear to be Ni as verified by energy dispersive spectroscopy.

GROOVE ADHESION TESTING AND SEM/EDS

The cold sprayed sample was subjected to groove adhesion testing. Groove testing was performed in compliance with ASTM Designation B 571 - 91 “Standard Test Methods for Adhesion of Metallic Coatings”. The schematic given in Figure 9 illustrates the geometry of the groove test. Two adjacent grooves are cut through the sample and the specimens are subsequently analyzed in the SEM for failure. A few caveats that must be kept in mind are that groove testing is more severe for thick coatings vs. thin coatings and much more severe for hard coatings vs. soft coatings. For soft coatings, the coating tends to plastically deform readily, which results in less shear stress being transferred to the substrate coating interface.

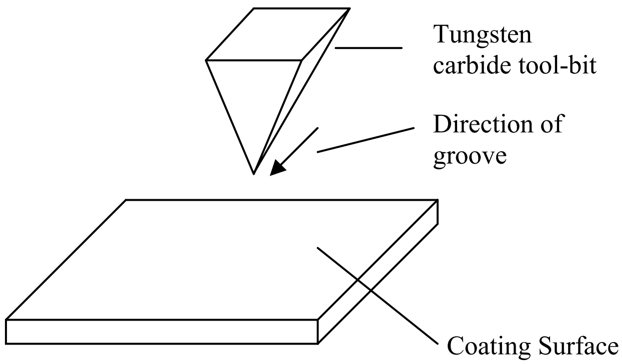

Figure 9. Schematic of groove adhesion test and orientation.

Given below are SEM images of the sample subjected to groove testing. Figure 10 (a) illustrates an area where the coating remained generally intact with only small areas of cohesive failure while Figure 10 (b) is near the unsupported edge of the sample where large areas have failed at the Ta-Ni interface on both the left side of the groove and in between the grooves.

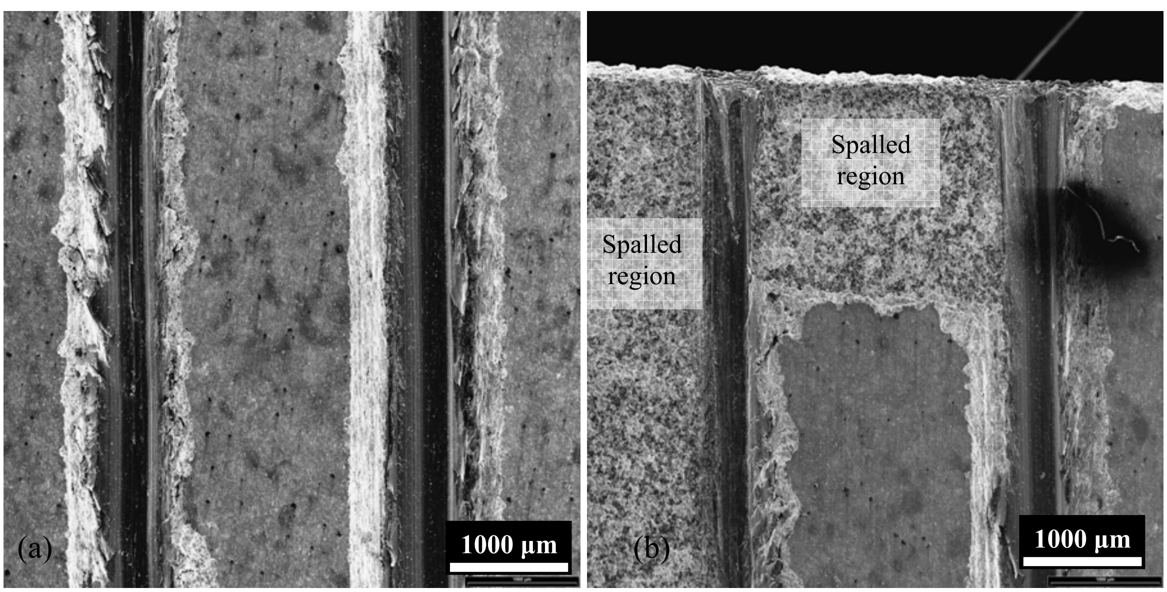

Figure 10. SEM images of the surface of the sample subjected to groove adhesion testing where (a) the coating remained primarily intact and (b) the coating failed catastrophically.

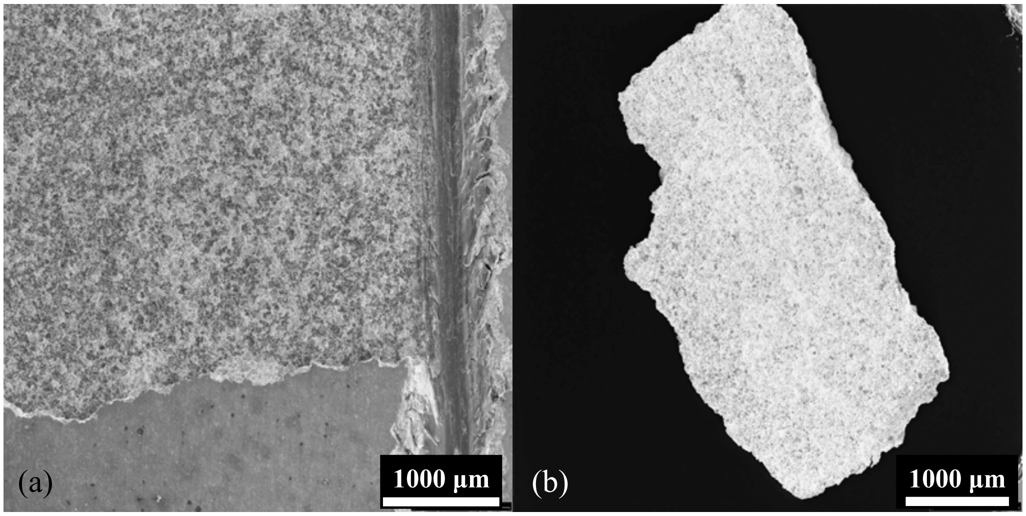

Figure 11. SEM micrographs of (a) the surface of the failed region and (b) the underside of the recovered chip.

A chip was recovered from one of the spalled regions. Both the surface of the spalled region and the mating surface on the underside of the recovered chip were analyzed via EDS to determine the exact nature of the failure.

EDS was used to determine whether the failure was primarily adhesive (interface) or cohesive (within coating or substrate). Figure 12 shows high magnification images of the surface and underside of the chip. Inset are EDS maps of the images showing composition. For Figure 12 (a), the yellow indicates Ni while the dark areas indicate Ta. For Figure 12 (b) the blue indicates Ta while the dark areas indicate Ni. Based on the mixture of Ta and Ni on both areas, it can be inferred that failure most likely originated within regions where the interface was porous and continued to fracture cohesively through the two materials where they are well bonded. A greater percentage of Ta is present on the Ni substrate than Ni on the Ta chip, indicating that cohesive fracture occurred primarily through the Ta. This is not surprising since the Ta was demonstrably more porous based on metallographic analysis, which would yield a lower fracture strength.

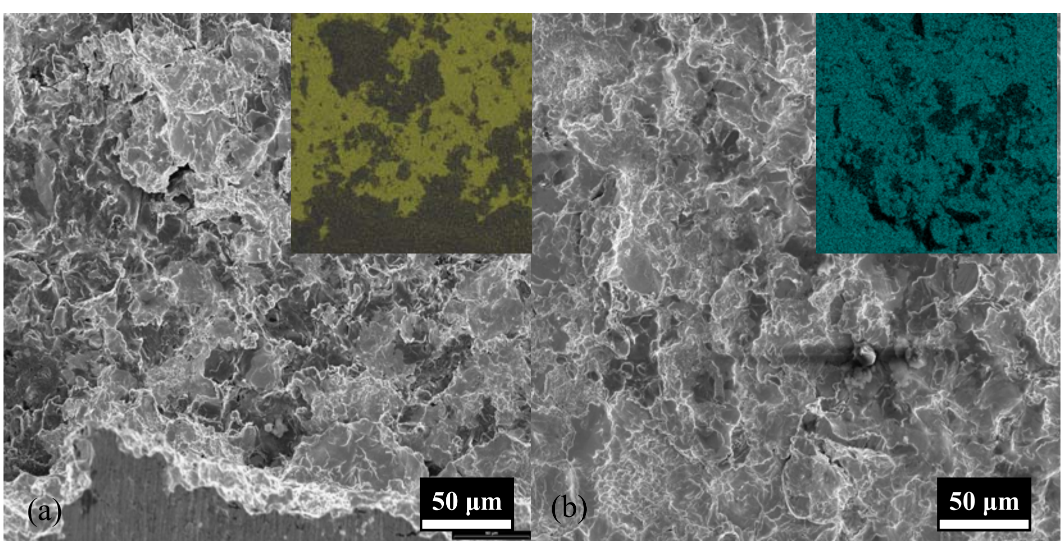

Figure 12. SEM micrographs of (a) the surface of the failed region and (b) the underside of the recovered chip. Inset are the EDS maps of the same.

In addition to the EDS analysis of the areas subjected to groove adhesion testing. The as-deposited surface was also analyzed to verify the composition of the inclusions observed in cross-section. The grinding marks are clear on the surface of the Ta and Ni inclusions which give a good contrast between the two materials as illustrated inset in Figure 13. The red in the EDS map of the image given in Figure 13 (b) indicates Ta while the green indicates Ni. As expected, the inclusions within the coating are indeed Ni.

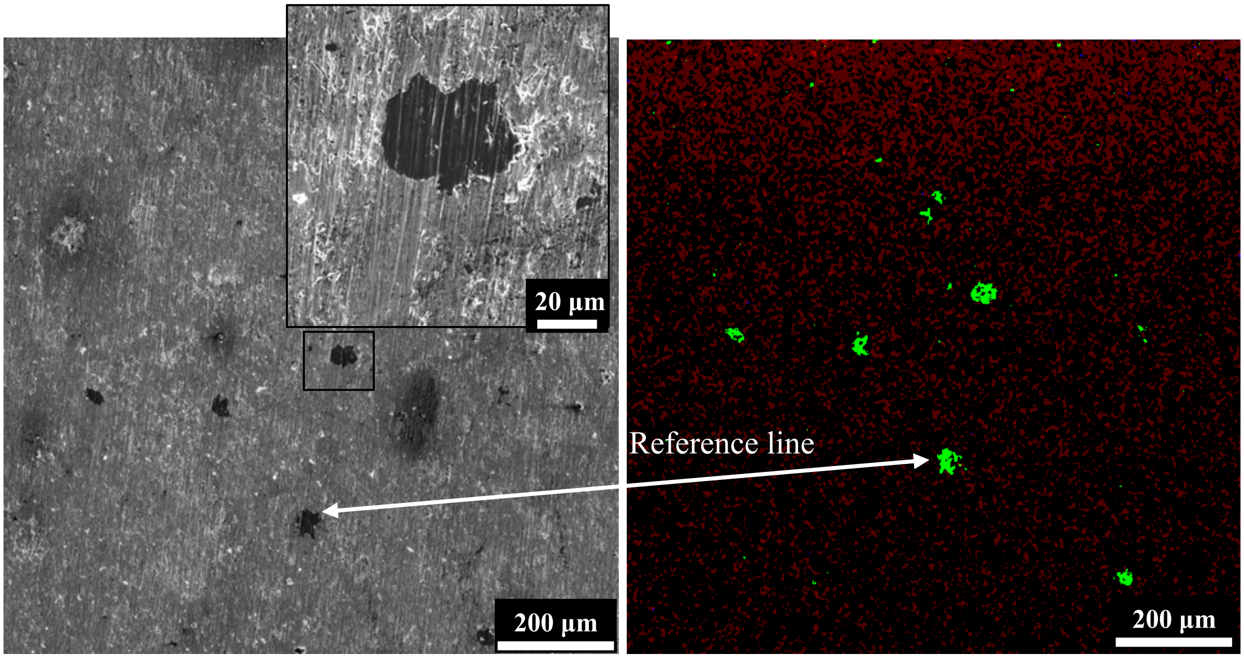

Figure 13. (a) SEM micrograph of the surface of the as-deposited cold spray coating and (b) an EDS map of the same region illustrating presence of Ni inclusions.

SUMMARY/CONCLUSIONS/RECOMMENDATIONS

- Two tantalum over nickel multilayer cold spray deposited samples were provided by ARL for analysis.
- Cold spray was demonstrated to be capable of depositing thick multilayer claddings (>1mm total thickness).
- The Ni bond-coat cladding is much denser than the Ta top-coat most likely due to the differences in density, melting point, and crystal structure (FCC Ni vs. BCC Ta). Perhaps modifying parameters such as particle velocity and temperature may alleviate these effects.
- The Ni-steel interface was much denser than and contiguous than that of the Ta-Ni. This is due not only to the issues mentioned above but also to the fact that the Ni makes for a harder, more impact resistant substrate than the underlying steel. The porosity of the Ta-Ni interface resulted in failure during groove adhesion testing.
- The ferritic steel structure is softer than tempered martensitic gun steel which may have further enhanced adhesion of the Ni bond-coat in the samples studied. It is recommended that further tests be completed on gun steel to analyze this effect.
- The structure of the Ni bond-coat is more homogenous than that of the Ta. The Ta actually contains large interspersed zones of Ni possibly due to Ni contamination within the cold spray nozzle.

- The hardness of the Ta is much higher than bulk or work-hardened Ta indicating the possible incorporation of impurities or an alloying effect with the co-deposited Ni.
- Catastrophic failures during groove adhesion testing give evidence that the transient thermal stresses generated during gun firing would act to spall the porous Ta coating.

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[1] Z. B. Zhao, B. A. Gillispie, and J. R. Smith, "Coating deposition by the kinetic spray process", *Surface and Coatings Technology*, vol. 200, no. 16-17, pp. 4746-4754 (2006).

[2] S. V. Klinkov, V. F. Kosarev, and M. Rein, "Cold spray deposition: Significance of particle impact phenomena", *Aerospace Science and Technology*, Vol. 9, no. 7, pp. 582-591 (2005).