Ceramic Materials
Testing and Modeling

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Ceramic Materials Testing and Modeling

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Purpose of this report: To fulfill requirement WP605BM4, provide Input to PA Design - Ceramics (WBS 1.2.2.5.7) and provide input for EMCR

Topics to be covered include the following: Thermal Spray Process, Coating Performance Model, Material Evaluations and Characterization, Corrosion Studies and Phase Transition Studies.

Introduction:
Certain refractory ceramics (notably oxides) have desirable properties suitable for the construction of ceramic waste containers for long term use in nuclear waste disposal applications. In particular, they are far less prone to environmental corrosion than metals under realistic repository conditions. The aqueous corrosion rates of oxides such as magnesium aluminate spinel (MgAl₂O₄) and alumina (Al₂O₃) fall in the range of a few millimeters per million years. Oxide ceramics are also not likely to be subject to microbiologically influenced corrosion, which apparently can attack most, if not all, of the available engineering metals.

Ceramics have a reputation for poor mechanical performance and large, impermeable objects are not easily fabricated by most current fabrication methods. As a result, the most promising approach for incorporating ceramics in large waste packages appears to be to apply a high density ceramic coating to a supporting metallic structure. Ceramic coatings applied by a thermal spray technique can be made effectively seamless and provide a method for final closure of the waste package while maintaining low average temperatures for the entire assembly. The corrosion resistance of the ceramic should prevent or delay water penetration to the underlying metal, which will in turn provide most of the mechanical strength and toughness required by the application. In this way, the major concerns regarding the ceramic coating become ensuring it is impervious to moisture, its adherence and its resistance to mechanical stresses during handling or resulting from rock fall in the repository. Without water, electrochemical corrosion and microbiologically influenced corrosion processes are considered impossible, so a complete coating should protect the metal vessels for far longer than the current design requirements. Even an imperfect coating should extend the life of the package, delaying the onset and reducing the severity of corrosion by limiting the transport of water and oxygen to the ceramic-metal interface.

Thermal spray techniques for ceramic coating metallic structures are currently being explored. The mechanics of thermal spray resembles spray painting in many respects, allowing large surfaces and contours to be covered smoothly. All of the relevant thermal spray processes use a high energy input to melt or partially melt a powdered oxide material, along with a high velocity gas to impinge the molten droplets onto a substrate where they conform, quench, solidify and adhere mechanically. The energy input can be an arc generated plasma, an oxy-fuel flame or an explosion. The appropriate feed material and the resulting coating morphologies vary with technique as well as with application parameters. To date on this project, several versions of arc plasma systems, a detonation coating system and two variations of high velocity oxy-fuel (HVOF) fired processes have been investigated, operating on several different ceramic materials.
For any given material, the choice of process, initial particle size and process parameters is largely a heat transfer issue. Particle size has much to do with it, since particles which are too coarse may not melt at all in the short time available for heat transfer while particles which are too fine may actually bounce off the spray plume and never get even close to their melting temperatures. Either type can still become entrained in the coating, leading to defects and porosity. Semi-molten particles can quench without fully conforming to the site of impact. Shadowing effects due to uneven coating build rates, uneven gas streams and so forth can also contribute defects.

Thermal spray of ceramics requires maintaining a balance between droplets which are too hot (significantly above the melting temperature) which may rebound upon impact prior to solidification or simply vaporize and those which are too cold (not molten). The various spray techniques are just different methodologies geared to getting more of the particles to the right state in order to deposit high density coatings with maximum efficiency and minimum defects. Detonation spraying uses explosive gas velocity for great impact energies but (relatively) low particle temperatures, counting on mechanical deformation to help achieve high coating density. High power plasmas heat the particles at very high currents under the premise that the higher the local energy density, the more particles will be heated to the correct temperature. Axial injection plasma systems introduce the particulates to the center of the flame, preventing them from bouncing off the plume and increasing dwell time in the flame. HVOF systems use high flame temperatures and high velocities to achieve performance. Each spray technique has an optimum particle size for each material being sprayed. The available powders are not necessarily identical and unfortunately not all materials are readily available in appropriate particle sizes. Some control of spray conditions is possible to allow for variations in particle size and composition, but good coatings do not generally result from a random pairing of powder and process.

**Coating Modeling:**
A model was developed to account for corrosion protection of steel by a thermal sprayed ceramic. This model accounts for increased impedance to oxygen transport due to a porous ceramic coating and a consequent reduction in corrosion rate. As part of this model, a quantity “g” is defined to account for pore geometries and pore fractions. The model also accounts for expansion (strain) of the coating due to the accumulation of corrosion products at the ceramic-metal interface to predict the onset of cracking required for spallation. It does not predict the ultimate degree of the potential spallation or its specific location. The model has been documented and appears at the end of this report.

Some important considerations:

1) The substrate corrosion mechanisms are not going to be changed by the presence of the coating, just slowed by reduced transport rates. If a substantial portion of a coating just disappeared, the situation would be no worse than it would have been without a coating. The metallic corrosion modeling presently being done would apply, just over a limited region which can be treated statistically.

2) In the example calculation presented in the model documentation, aqueous corrosion rates at the substrate are reduced from 300 μm/y to 8.6x10⁻² μm/y. The model treats the ceramic coating as an isotropic continuum and treats the waste package in its entirety in

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order to predict the onset of the first crack in the coating. This allows a very conservative estimate of an additional 14,000 years of life for the CAM in a saturated environment. The formation of a single crack would not constitute total failure and removal of the coating, although it would tend to relieve stresses that might lead to further cracking.

3) The uncorrected g-factor is an estimate applied to compensate for the effect of a porous coating on the transport of oxygen to the metallic substrate. Logically, if the oxygen transport is impeded, the corrosion rate will decrease. The uncorrected g-factor is based on the presumption of a simple cylindrical pore geometry. The "corrected" g-factor accounts for the influence of more realistic pores. An idealized version of a real pore geometry consists of a series of spheres, which dominates the total pore fraction, and a series of smaller interconnecting cylinders, which dominates the impedance to oxygen transport. In describing the pores mathematically, regular forms are a convenient fiction, just as they are in particle size measurement. Particle size distributions are reported in terms of "equivalent spherical diameter" because it is mathematically intractable to describe each of the billions of particles exactly, nor is it necessary when describing an average behavior. The same applies to pores and channels which are uniformly distributed throughout a coating. The model calculation is highly sensitive to the values assigned to the pore parameters, especially the cylinder diameters. The example pore dimensions used to illustrate the model were not rigorously determined so the explicit results can not yet be trusted for accuracy. Likewise, the value of elastic modulus used in the failure calculation was taken from the literature. Each of these quantities will need to be determined experimentally.

4) The impedance to oxygen transport imposed by a porous coating depends upon whether the pores are filled with liquid, gas, or an appropriate sealant. In order to be conservative, the g-factor for dry oxidation was assumed to be unity due to unsealed, gas-filled porosity. Effectively, the ceramic was ignored for dry oxidation, even though something like 98 percent of the substrate surface is covered and the remainder is exposed only through long, convoluted and narrow channels. The g-factor for aqueous phase corrosion will necessarily be much smaller than this, due to reduced diffusion rates of oxygen through liquid filled pores. The g-factor for the humid air corrosion regime is the largest source of uncertainty and is simply assumed to lie somewhere between the g-factor for dry oxidation and that for aqueous phase corrosion. In the absence of conclusive experimental data, the uncertainty in the g-factor for this regime could easily be several orders of magnitude.

Materials Under Test
Based on a prior literature and vendor study\(^2\) the coating materials initially selected for experimental tests were magnesium aluminate spinel (MgAl\(_2\)O\(_4\)), aluminum oxide (Al\(_2\)O\(_3\)), titanium dioxide (TiO\(_2\)) and a few combinations of these materials. Combinations of materials are reported to result in improved toughness when the materials are co-sprayed, otherwise the chemical and structural properties resemble the pure oxides. Each ceramic being considered is a chemically stable oxide with good corrosion resistance, naturally occurring analogs and no glassy component. Each melts at about 2150°C or less. Alumina and titania were chosen based on solubility studies\(^3\) performed in Sweden during the late 1970's which suggested that either material is likely to survive more or less indefinitely in contact with water underground. Their dissolution rates in aqueous corrosion are on


the order of a few millimeters per million years. The spinel was originally chosen because of its extreme radiation tolerance, chemical resistance and similarity to alumina in working properties. Stabilized zirconia ($\text{ZrO}_2$) is another ceramic which has been considered as an additional option, although it is not actively being pursued in the current work due to the increased difficulty of producing dense coatings with such a refractory material (melting point >2700°F).

Of the materials being tested, alumina is the most common commercially and somewhat stronger than the others, but its thermal sprayed form is subject to a phase transition which could possibly cause cracking over time. As part of the initial experimental work at LLNL, the tendency for this transformation to take place over long times at moderately elevated temperatures was verified during a year long thermal treatment study. As a result, it was eventually concluded that spinel offers the best combination of physical properties, since it does not have a metastable form which might transform after spraying.

**Test Methods**
The major analytical methods used in this assessment are (1) Metallography (to evaluate coating structures, total porosity and corrosion behavior) (2) Adhesive/cohesive bond strength measurements, (3) impact testing (to simulate rock fall) and (4) AC impedance spectroscopy (to estimate the resistance to oxygen transport through a porous ceramic coating. Additional analytical techniques used include X-ray diffraction, scanning electron microscopy and die penetrant examinations.

**Sample Types**
Three general configurations of ceramic coated carbon steel samples have been used in the work done to date. Flat plate samples (various sizes) are examined using die penetrants and sectioned to evaluate the structures of the ceramic coating. Larger versions are used for impact studies. Smaller versions are used for x-ray diffraction and heat treatment studies. Flat ended bond strength coupons (1” in diameter) conforming to ASTM C633-79 are used to measure the adhesive/cohesive strength of the coatings on their substrates. Corrosion test coupons (6” long by 1” diameter) are cross sectioned following exposure to various environmental conditions to locate and measure corrosion products at the ceramic-metal interface. Some of these samples are deliberately damaged by slicing with a diamond saw prior to corrosion testing in order to expose a portion of the substrate. This same sample type is sectioned for AC impedance measurements and allows a modified version of the adhesive/cohesive bond strength test to be conducted following corrosion testing.

**Process Evaluation and Characterization:**
For this study, conventional arc plasma generated alumina coating samples on steel were produced in-house at LLNL, of various materials at Vartec Inc., a commercial coating service and more recently of spinel at the Idaho National Engineering and Environmental Laboratory (INEEL). The work at INEEL was contracted directly by the M&O. Samples of HVOF alumina-titania and spinel coatings produced using hydrogen as a fuel were purchased from Vartec. Detonation sprayed samples of alumina, titania and spinel were purchased from Demeton America Inc., an equipment manufacturer. Samples of various materials produced using an axial injection plasma spray technique have been ordered from Northwest Mettech, another equipment manufacturer. The Center for Thermal Spray Research at Stony Brook declined to provide samples coated using a water stabilized plasma system on the grounds that coatings produced by that technique can be manufactured quickly but are not particularly high in density.

**Status of ordered samples as of 4/30/98:**
All samples ordered to date from Vartec and Demeton have been delivered and are being tested. These orders did not include ASTM style test coupons. One full set of plasma sprayed spinel samples with no bond coat was delivered by INEEL out of 6 different sets.
originally requested. The corrosion style coupons they delivered were uncoated at the ends. As part of a subcontract with INEEL, TAFA has delivered two full sets of cylindrical specimens (with and without bond coat) produced using a high power plasma (“Plazjet”) system. These samples also have uncoated ends. TAFA has not yet delivered any flat plate or mechanical test specimens. Since they use propylene as a fuel, TAFA tried but was unable to coat any specimens with spinel using their HVOF system, also as part of work subcontracted by INEEL. INEEL has issued a final report\(^4\) based on their own development work and the work at TAFA. All remaining undelivered samples are approximately one month past due.

**Bond Coats**

Some coating samples were applied over a "bond coat" of a nickel based alloy resembling C-22. This was done to determine whether improved adhesion might result and possibly to limit an "expansion-upon-rusting" failure issue that was raised regarding the corrosion products generated by oxidation of steel. A counter argument has been suggested in that an inadvertent mechanical penetration of the coating and the thin nickel alloy bond coat could lead to the formation of an undesirable electrochemical potential, possibly accelerating local corrosion of the carbon steel CAM.

The presence of a bond coat also complicates the issues of package closure and re-work following any mechanical damage. If the patch was improperly prepared or executed, a situation could actually arise where a new portion of the bond coat would be applied over a portion of the undamaged ceramic. Such an overlap might or might not be dangerous, but is undesirable since it represents an unpredictable physical discontinuity. Similar objections can be raised regarding graded coatings since it is always difficult to blend the old with the new perfectly. If the limiting factor is the cohesive strength of the ceramic rather than the adhesive strength of the bond, bond coats and graded coatings may be superfluous.

**Metallography**

Optical and SEM metallography of sample cross sections demonstrate the morphology of the various coating types received. Image analysis was used to estimate the total fraction of porosity. Polishing reveals overlapping splat patterns quite well. There is usually a contrast difference between adjacent grains which may be due to differential polishing along different crystallographic axes. There is also some tendency for relief polishing to occur at the boundaries between grains. A few representative micrographs are included in this document. Figure 1 shows an optical micrograph of a low density (~19% porous) coating made via conventional plasma spray. The coating shown has been corrosion tested but the microstructure is unchanged.

Figure 2 is an example scanning electron micrograph showing the pore structure of a conventional plasma coating. In low density coatings particularly, large numbers of circular and elongated (sausage like) pores are visible between the flattened plates making up the coating. As would be expected, these elongated pores run more or less parallel to the substrate surface along the grain edges. Many of the apparently circular pores might just be the elongated type revealed in cross section. The lines of grains appear to undulate, probably due to the fact that each splat falls only partially over the others and to the varying sizes of the grains themselves. In places, there are radial separations (microcracks or pores) which appear to be sub micron in thickness and a few microns long (as long as the grains are thick) running between layers. Other interesting features include rounded inclusions

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particles which apparently melted but had resolidified before impacting the surface) and sharp edged inclusions (particles which apparently had never melted, but were merely trapped in the coating).

In high density coatings (i.e. HVOF), the splats are less obvious, but still visible at high magnification due to contrast differences. An optical cross section of an HVOF type coating is shown in Figure 3. Figure 4 is an SEM image showing the finer grain and pore structures in an HVOF coating. There are still pores in evidence, but far fewer and with less obvious links between them. Many of the pores appear to be equiaxed (sphere-like). There is still some evidence of inclusions, but far more of the rounded variety than the sharp ones.

Figure 5 shows an optical micrograph provided by INEEL representing the structure of a conventionally plasma sprayed spinel coating produced at their facility. Figure 6 is an optical micrograph also provided by INEEL showing a high density coating produced at TAF using their ‘Plazjet’ high power coating system. In both cases, INEEL reports porosities (measured optically) of less than 1%. These are comparable to the 2% porosity estimated for Vartec HVOF coatings, and in the case of the conventional plasma, quite an unexpected result. Porosity estimates made on the INEEL and TAF samples at LLNL are slightly higher (about 2%). Regardless of the exact number, this work has demonstrated that very high density ceramic coatings can be fabricated by several different thermal spray methods, without recourse to unconventional methods or diagnostic devices.

**Corrosion Testing**

Corrosion testing of ceramic coated coupons is being carried out under various conditions, but especially in the LLNL long term corrosion test facility. Initially, sets of six coupons coated with plasma sprayed alumina and an HVOF sprayed alumina-titania composite were placed in one of the tanks containing simulated 10X concentrated J-13 well water at 90°C (total dissolved solids ~1500 ppm, pH between 10 and 10.2). The samples were placed straddling the water line, exposing them to water, oxygen and deposited salts due to evaporation, which should be the most corrosive conditions likely to occur. Six of each type of sample were put in whole and six of each were deliberately slotted in two places (above and below the water line) to induce corrosion damage underneath the coatings. Figures 1 and 3 show samples which have undergone testing for 6 months in this environment.

At various intervals and as they become available, additional sample materials applied via the various thermal spray techniques have been emplaced in the corrosion tank described above as well as in a tank containing water acidified to pH 2.7 using organic acids. These later samples have primarily been coated with spinel, although given the long lead times involved in ordering large numbers of small coated parts, some samples which have yet to arrive will still be coated with other materials. Humid air corrosion (HAC) tests are planned in humidity chambers currently being used to evaluate HAC of uncoated metals. Samples of several different types are available for this purpose. As of 4/30/98, the racks ordered to support them have not been delivered.

Samples have been withdrawn from the corrosion baths at intervals for examination. Prior to sectioning, the slotted regions are filled with epoxy to trap any corrosion products which might be present. They are then sectioned across the slot and polished. The substrates are etched with Nitol to reveal the grain structure. Metallography of 10 ceramic coated samples tested for periods of 3 and 6 months in simulated 10X concentrated J-13 water was completed on 4/28/98. Cross sections of several of these samples are shown in Figures 1, 3, 7 and 8.
As might be expected, highly porous coatings (~19% porosity) afforded incomplete corrosion protection. As shown in Figure 7A, these coatings were subject to spallation near the slot. In some places away from the slot, it appeared that the substrate was not corroded at all, although there were also places in unslotted samples where the corrosion was relatively thick (>0.1 mm) as shown in Figure 1. This is comparable to the thickness of the corrosion actually observed inside the slot, which was unprotected. The corrosion adjacent to one side of the slot was thick enough to cause spallation and appeared to penetrate quite deeply along the interface (>1 cm). On the other side of the slot, the corrosion layer was thinner (~0.05 mm) and did not penetrate as far along the interface (~0.3 mm). This suggests that the coating properties were highly variable or that the coating was stressed and partly separated from the substrate by the slotting operation prior to corrosion testing.

Dense HVOF (~2% porous) and detonation (~6% porous) coatings are shown in Figure 7B and Figure 8. One of the detonation coatings has a nickel based bond coat. All three of these coatings gave significant corrosion protection, with no apparent corrosion of the substrates detected anywhere except where they had been deliberately exposed by slotting. There was significantly more corrosion apparent in the sample with the bond coat than without, possibly resulting from an electrochemical interaction. There was no apparent undercutting of any of the dense coatings by corrosion, suggesting that penetration of oxygen beneath a properly applied, dense coating is very slow.

Corrosion products seemed to accumulate in the slots (~0.3 mm wide) on several samples, apparently causing a plugging effect. There is nothing conclusive about this, but it suggests that minor defects in otherwise high quality coatings might be self limiting to some degree, as long as there was no mechanism to remove the corrosion products.

**Contact Conductivity and AC Impedance Spectroscopy**

Using a millivolt source, simple contact conductivity (DC resistance) measurements were made on high porosity plasma (~19% porous) and low porosity HVOF (~2% porous) coated samples immersed in distilled water. When the electrodes were applied to a dry coating, the DC resistance was effectively infinite in both cases. Upon the addition of water, the more porous coating achieved a minimum resistance of several tens of ohms, which increased within minutes to a few hundred thousand ohms. The denser coating offered a minimum resistance of a few hundred thousand ohms which increased over a slightly longer time to several megaohms. The behavior was the same regardless of polarity. There was considerable difference in the time of response and the low and high resistance values achieved, but it was clear that a conductive pathway to the substrate was established quickly in each case. It was not clear from this simplistic test whether the increase in apparent resistance was the result of polarization, nor how much of the substrate surface was actually exposed.

Alternating current (AC) impedance spectroscopy was then carried out using a potentiostat on several variations of thermal sprayed samples following a technique described by Farmer⁵. Measurements were made on samples with: (1) no coating (2) ~2% porous coatings (3) ~6% porous coatings and (4) ~19% porous coatings immersed in simulated concentrated J-13 water (~130,000 ppm dissolved solids). There was some variability in the exposed sample size for these initial tests, making it difficult to distinguish quantitatively between the two high density coated samples, but a standard preparation method has now been selected to eliminate this experimental variability from future tests. A graph of the experimental results is shown in Figure 9.

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The impedance of the denser coatings was approximately 8 orders of magnitude greater than that of the bare substrate at low frequencies and 4 orders of magnitude greater at high frequencies. The highly porous coating behaved much like the bare substrate, which was not surprising, since metallography of this type coating clearly shows large scale interconnected porosity. Six percent porosity is the normally accepted division point between interconnected and fully isolated porosity. This is a “rule of thumb” regarding isotropic sintered materials rather than highly oriented materials produced by other methods, but comes close for most ceramics.

Since electrical conductivity through liquid filled channels is directly related to the ease with which various species (including dissolved oxygen) can pass through the channels, the electrical impedance measured at low frequencies should correspond directly to the impedance of oxygen transport from the outside to the substrate. An 8 order of magnitude increase in impedance corresponds to an 8 order of magnitude reduction in oxygen transport rate and therefore represents an 8 order of magnitude reduction in corrosion rate compared to the uncoated condition. These results are in agreement with the physical observations of the lack of corrosion detected beneath dense coatings in the long term test. At high AC frequencies, there is still electrical conductivity due to charge transfer, but one can picture the ions themselves merely oscillating in place, so that there would still be reduced net transport of oxygen to the substrate.

Impact Studies:
Due to the possibility of point loads during handling and as a result of rock falls, the robustness of coatings on waste containers was evaluated qualitatively using drop tests on alumina coated steel substrates. Various plasma coated blocks 4” thick were impacted from a height of up to 2.5 meters using a 100 kilogram load. This would be equivalent to a rock slightly larger than 1 cubic foot in size falling from a similar distance. Rounded and pointed impactors were used to simulate the most likely extremes of shapes to be encountered during a rock fall. Metallic impactors were deemed unsuitable because their elastic and fracture response would be quite different from those of the natural rock. Instead, porcelain tipped impactors that closely match the average chemistry and physical behavior of the Yucca Mountain welded tuff were used.

Surrogates were needed because of the wide variability in the physical properties of the natural material, combined with the expense of producing specific shapes by machining of rock. The impactors were cylinders 2” diameter by 4.5” long, with shaped ends. While the chemical composition is relatively easy to reproduce using a porcelain body (clay, flint, feldspar) obtaining a matching load/unload pulse during impact is more difficult. A reasonable match to the pressure pulse caused by impact of the natural material was achieved by varying firing conditions to control the total porosity of the porcelain impactors.

The nose configuration of the impactor plays a significant role in whether the coating will maintain its integrity under impact. As might be expected, a pointed nose appears to be the worst case, causing chipping of the coating under relatively low kinetic energies. Any impact which permanently deformed the underlying substrate caused the coating to fracture over the deformed area. Most fractures penetrated part way into the coating, leaving some protection, although a few actually exposed bare metal. No extended cracking or collateral damage of the coating outside the impact zone was observed and there did not seem to be any difference in behavior when impacts were repeated on adjacent areas of samples previously tested.
Mechanical Test
ASTM test procedure C633-79 measures the "adhesive/cohesive" strength of the coatings. This procedure is being used to establish a base line for bond strength of coatings prior to corrosion testing. A modified pull test using pins with somewhat smaller dimensions than called out in the standard is being used on corrosion style coupons to determine the bond strength after exposure. This test is being calibrated against the ASTM configuration. So far, only HVOF samples from Vartec and plasma coatings generated at LLNL have been mechanically tested. As of 4/30/98, one set of ASTM style samples with no bond coat had been delivered by INEEL, although that organization reported a bond strength of approximately 1900 psi with and without a bond coat during their internal testing. This result has not yet been confirmed by LLNL, since comparable samples with a bond coat have not yet been shipped. Neither have additional samples that INEEL subcontracted to TAFA nor others being fabricated by Northwest Mettech.

The open literature reports that (for spinel), a nickel based bond improves the overall strength measured on steel substrates. In reality, failure occurs at the weakest link in the chain being tested. That could be the metal to metal bond (where a bond coat is used), the ceramic to metal bond, the adhesive bond used to attach the test fixture or within one of the layers. So far, the samples tested in this study have almost all failed at the glue bond (up to about 5000 psi), leaving the coating intact. The only exception was a case where the pull pin was inadvertently bent sideways as it was pulled, in which case a portion of the coating adhered to the pull pin and separated from the sample in shear. Only a few layers of particles adhered to the pin, the coating did not fail down to bare metal. There was no separate bond coat in this case.

A possible implication of this lone discrepancy (although this is not proven) is that the bond between either metal phase and the ceramic will be stronger than the interparticle bonds within the ceramic coating. If this is true in all cases, then for thick coatings in particular, the measured strength will always be limited by the ceramic cohesion rather than the adhesion (if not by the adhesive used in the test). This is a logical assumption because unlike ceramics, metals are able to deform plastically even when spray conditions are not ideal, producing more complete conformance to previous layers. It may not be necessary to worry about the strength of the ceramic to metal bond, as long as it is stronger than the strength of the coating itself.

It should be noted here that the adhesive used in most of the testing done to date is not one of the specific filled epoxy products listed in ASTM test procedure C633-79. None of the listed products was available. The manufacturers of the nearest equivalents list their average tensile strength at 2300 psi, which is only about half of what the standard suggests they should be. This seems to be an inconsistency in the standard, although it is possible that fresh batches of the filled adhesive actually match the performance cited by the ASTM. A pure resin system based on Epon 815 was substituted, resulting in stronger adhesion, but there is some concern that the unfilled adhesive could penetrate porous coatings and skew the results. Newer filled epoxy adhesives with a reported adhesive strength of about 12 to 15 ksi are on order from Masterbond Adhesives.

Thermal Cycling
Coated corrosion style coupons were rapidly cycled five times between ambient temperature and 400°C at a rate of about 100°C/hr with no apparent effect on the coatings. This is a higher temperature and far more rapid cycling than could take place in the repository, which is expected to heat and cool over a span of years. Samples were thermal shock tested by heating to temperatures as high as 600°C and quenching into either room temperature or boiling water, again with no discernible effect. This is consistent with (and
far more severe than) thermal stress modeling\(^6\) results which suggest that residual stresses in ceramic coatings due to heating by emplaced waste should be insufficient to materially affect the bond strength, even at the large sizes projected for the waste packages.

**Interim Conclusions**

HVOF using hydrogen as the fuel source has provided the most successful thermal sprayed ceramic coatings tested to date. Metallography of INEEL plasma and TAFA “Plazjet” samples shows that these techniques are also capable of producing high density coatings. Detonation coated samples are slightly lower in density, but offer similar impedance to oxygen transport.

A model has been developed to account for reduced corrosion of metallic substrates by porous ceramic coatings. Predictions of significantly increased corrosion lifetimes are supported by preliminary corrosion test results and by AC impedance spectroscopy which demonstrates an 8 order of magnitude increase in impedance, corresponding to an 8 order of magnitude decrease in oxygen transport through low porosity coatings.

Nickel based bond coats may actually degrade corrosion protection of steel substrates due to electrochemical effects in the event that the coating and bond coat are inadvertently damaged.

**Future Work**

Immediate future goals of this project are to complete the planned evaluations on the various purchased samples as they arrive. More extensive AC impedance measurements will be carried out, including materials which have been sealed using various inorganic and metallic sealant materials. If the corrosion work continues to be as promising as early results indicate, there will be a shift toward use of larger samples in order to demonstrate that high density coatings can be applied to larger surfaces more closely resembling the proposed waste package designs. An attempt will be made to apply non destructive evaluation (NDE) techniques to larger coated surfaces and determine the size and severity of flaws which may be buried in the coatings. Various methods will be used to artificially implant flaws of various sizes in known locations. Possible artificial flaws include:

1) overcoating of materials glued onto the substrate or onto a partially complete coating
2) rubbing solder onto a partially complete coating with a hot iron
3) impacting the coating with a center punch prior to spraying over with a final coat
4) deliberately forming a heavy rust scale on a portion of the substrate
5) rubbing areas with a refractory cement prior to coating
6) drilling holes in the substrate parallel to the coating.

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Figure 1: Porous plasma sprayed alumina coating after 6 months in 10X concentrated simulated J-13 water at 90°C
Figure 2: SEM micrograph showing the structure of a plasma sprayed coating
Figure 3: Dense HVOF sprayed alumina-titania coating after 6 months in 10X concentrated simulated J-13 water at 90°C
Figure 4: SEM micrograph showing the structure of an HVOF sprayed coating
Figure 5: Optical micrograph of spinel coating deposited using Metco 9MB torch (INEEL)
Figure 6: Optical micrograph of spinel coating deposited using TAFA "Plazjet" (INEEL)
Figure 7: Optical micrographs showing 19% porous plasma sprayed alumina and 2% porous HVOF sprayed alumina-titania after 6 months in simulated 10X concentrated J-13 water at 90°C (slotted samples)
Figure 8: Detonation sprayed alumina coatings with and without Ni bond coat. Tested for 3 months in simulated concentrated J-13 water at 90°C
Figure 9: AC impedance measurements of ceramic coatings made by various thermal spray techniques