# B. Thick Thermal Barrier Coatings for Low-Emission, High-Efficiency Diesel Engine Components

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## Objectives

- Develop new approaches to coating design and fabrication to aid in overcoming hurdles to the durability of thermal sprayed coatings. Specific objectives are these:
  - — Develop the laser technology of surface dimpling, cleaning, and laser-assisted spraying to enhance adherence and increase coating strength.
  - — Develop phosphate-bonded composites for thermal management coatings.
  - — Evaluate quasicrystalline materials as potential thermal barrier and wear coatings.

## Approach

- Conduct an initial cost assessment for the laser processing to assess the potential for commercialization; the most cost-effective processes will be evaluated for potential impact on coating adherence.
- Measure the mechanical and physical properties of phosphate-bonded composites to determine their potential for use as thermal barrier coatings (TBCs).
- Evaluate the thermal stability of quasicrystalline materials at engine operating temperatures by means of diffusion couple experiments.

## Accomplishments

- Completed cost analysis of laser pre- and post-treatments and selected post laser “tacking” as the method for treating coatings to increase adherence.
- Developed phosphate-bonded composite coatings that survived initial thermal cycling to 650ºC with good residual adherence to the substrate.
- Sprayed quasicrystalline coatings using the high-velocity, oxygen-fueled (HVOF) technique and began evaluating their thermal conductivities.

### Future Direction

- Laser-tack tensile adhesion specimens to evaluate the potential strength increase produced. Review laser-assisted thermal spraying results with Fraunhofer USA, which holds patents in this area.[1] Couple a laser with plasma spraying if the review with Fraunhofer shows promise.
- Further evaluate phosphate-bonded composite coatings under thermal cycling with higher thermal gradients and a greater number of cycles.
- Evaluate diffusion couples of quasicrystalline coatings for coating stability at temperatures ranging from 600 to 900°C. Evaluate bond coating chemistry effects on the diffusion of the quasicrystalline alloy elements.

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## Introduction

Engine testing of thermal sprayed coatings has demonstrated their potential benefit as TBCs and wear coatings to reduce fuel consumption, wear, and component temperatures.[2–4] The durability of thermal sprayed coatings, particularly TBCs, remains the major technical challenge to their implementation in new engine designs. New approaches to coating design and fabrication will be developed to aid in overcoming this technical hurdle.

## Laser Technologies

Three basic areas of laser-augmented spray coating work are evaluated:

1. Laser roughening: A substrate is roughened via laser machining prior to spray coating to create mechanical interlocking for better adhesion capability.
2. Laser-assisted spray coating: A laser assists the spray coating by optically striking airborn spray particles or freshly embedded particles with relatively low peak power density.[5]
3. Laser tacking: Laser pulses penetrate through the coating and into the substrate during processing to create occasional metallurgical bonds.

## Phosphate-Bonded Composites

Phosphate-bonded composites consist of filler material bonded together by a phosphate. The compositions of both the filler and the phosphate binder can be widely varied and, for this reason, so can the properties of the composite. Phosphate-bonded composites are well known and have been in occasional use for many years as refractory mortars and cements; high-temperature, corrosion-resistant coatings; temporary bone replacements; fast-cure paving cement; and dental cement.

The false-melt phenomenon of some phosphates was discovered at Caterpillar in 1994.[6] As the binder rises from room temperature to 150°C, unbonded water escapes, allowing the structure to collapse and become more rigid, like a sponge as it dries. Efforts on metal-phosphate composites at Caterpillar have been aimed at developing seal coatings, corrosion-resistant coatings, high-temperature adhesives, and, in the current study, thermal insulating coatings.

## Quasicrystalline Coatings

Quasicrystalline materials may provide advantages over ceramic TBCs because of their unique properties. The low thermal conductivity of some quasicrystalline materials approaches that of zirconia, and their thermal expansion is similar to that of steel, aluminum, and cast iron materials used in diesel engines. One of the major advantages in the use of the quasicrystalline materials based on aluminum is the ability to apply the coating via HVOF processing, thereby creating a coating with higher strength, higher adherence, and higher density. Coating structures produced using HVOF processes can have near 99% densities, compared with the 80–95% densities found in plasma-sprayed ceramic TBCs. Coating adherences of 65 MPa or greater are common for HVOF coatings, while the adherence of plasma coatings is generally less than 50 MPa.

## Approach

### Laser Technologies

Laser roughening, laser tacking, and laser-assisted spray coating of the substrates and coatings are being assessed for cost-effectiveness in the initial evaluation. The adherence of laser-treated coating will be measured using ASTM tensile adhesion testing techniques if the process is determined to be economically feasible.

### Phosphate-bonded Composites

Caterpillar's patented phosphate-bonded seal coating technology will be used with ceramic microspheres to develop new low-thermal-conductivity ceramic composites for use as TBCs. Coating the internal diameters of cylinder head ports and manifolds to reduce heat rejection is the main application of interest for these coatings. Mechanical and thermal properties of the composites will be evaluated and their stability assessed by thermal exposure and thermal shock testing.

### Quasicrystalline Coatings

One quasicrystal, with the stoichiometry $Al_{71}Co_{13}Fe_8Cr_8$, has previously been investigated for use as a TBC in aero applications and will be the starting point for this investigation.[7, 8] This alloy was reported to have a bulk thermal conductivity similar to that of zirconia and was shown to have good high-temperature oxidation. The main emphasis of the evaluation will be to spray the material using HVOF processing and determine its thermal stability at diesel component operating temperatures, using diffusion couple techniques.

## Results

### Laser Roughening

Laser roughening occurs when sufficient optical energy impinges a substrate to cause either ablation or homogenous boiling. In either case, the focused laser removes a small volume of material for each laser pulse. The micro-machining process takes place where the laser is focused on a very small spot (usually 25 microns in diameter) and requires that the beam be rastered to affect large surfaces, which can lead to long processing times and high cost.

Two basic types of pulsed lasers are potential candidates for laser roughening: femto-second lasers and UV nano-second lasers. Each of these lasers processes principally in the ablation regime. The femto laser creates ablation through a multi-photon interaction enabled by extremely high peak pulse power (1mJ/130E-15 sec = 7.5 GW). Conversely, the UV nanosecond lasers rely on the photon energy to initiate the ablation process. UV lasers are commercially available in 355 and 266 nm (frequency tripled and quadrupled Nd:YAG, respectively).

Table 1 compares the operational differences between the two systems and characterizes the small volume removal rates to be expected for this process. The economic merit of this process would have to be compared with the value it would provide relative to current process limitations and relative to alternative pathways to the same result through a lower-cost solution such as grit blasting, traditionally used to prepare surfaces for thermal spray coating. The most likely candidates would be small components with <1 $cm^2$ area to be roughened (i.e., fuel systems).

**Table 1.** Comparison of femto lasers and nano-second lasers

| Characteristic | Femto lasers | UV lasers |
|---|---|---|
| System size | 1,000 × 800 × 300 mm | 400 × 200 × 200 mm |
| Wavelength | 800 nm | 355 and 266 nm |
| Beam quality ($m^2$) | 1.2 | 1.1 |
| Laser average power | 1 to 3 W | 1 to 10 W |
| Laser cost | $250–300K | $125–150K |
| Material removal process | Ablation in vacuum; some plasma melting in ambient | 266—ablation 355—some ablation |
| Typical pulse duration | 130 femtoseconds (1E-15) | 15 nanoseconds (1E-9) |
| Peak power | ~1E-10 W | ~1E-5 W |
| Typical focus spot size | 25 microns | 10 microns for 266 |
| Peak power density | 2E-15 w/$cm^2$ | 2E-11 w/$cm^2$ |
| Depth removal/pulse | 0.5 micron | 1–2 microns |
| Volume removal/pulse | 150–200 $microns^3$ | 100–150 $microns^3$ |
| Pulse frequency | 5,000 Hz | 10,000 Hz |
| Volume removal/second | 0.0010 $mm^3$ | 0.0015 $mm^3$ |

## Laser-assisted Spray Coating

A laser assists spray coating by optically striking airborn spray particles or freshly embedded particles with relatively low peak power density. The purpose of the laser-assisted process is to provide shallow melting to create a completely dense coating with a metallurgical bond onto the substrate. Because the process requires relatively low power density (<1E-6 W/$cm^2$), there are several candidate lasers from which to choose. These are outlined in Table 2. Note that the final cost values are expressed in $/layer/$cm^2$. Costs in the range of $0.04 to $0.09 may be acceptable if the durability of the TBC can be increased.

## Laser Tacking

Unlike laser-assisted spraying, laser tacking would purposely exploit the laser key-holing phenomenon. Traditionally, either a $CO_2$ or YAG laser would be used for this process; the $CO_2$ laser is more economically viable. Two relatively new lasers are available—the direct diode laser and the fiber laser. The direct diode laser is cost-viable. However, the beam comes out as an approximately 3×12 mm rectangle; this is cost-competitive compared with the $CO_2$ laser, but it may tack down more than is necessary. In addition, the direct diode laser does not keyhole but is primarily used in the conduction weld (shallow melt) mode. The second new laser, the fiber laser, entered the kilowatt power range within the past year, with a few test lasers just becoming available. Currently, the cost for the fiber laser is prohibitive, but the costs will come down as the technology advances; the expected future costs are listed in Table 3.

## Phosphate-bonded Composites

Composites were produced using packed mullite hollow microspheres with a mean particle size of 150 µm as the main filler (Figure 1). The rest of the open volume was then filled with alumina, and the remaining space was filled with the Al-Cr-$P_2O_5$ binder. The thermal conductivity of the resulting composite was measured and is in the same range as plasma-sprayed TBC materials, as shown in Figure 2.

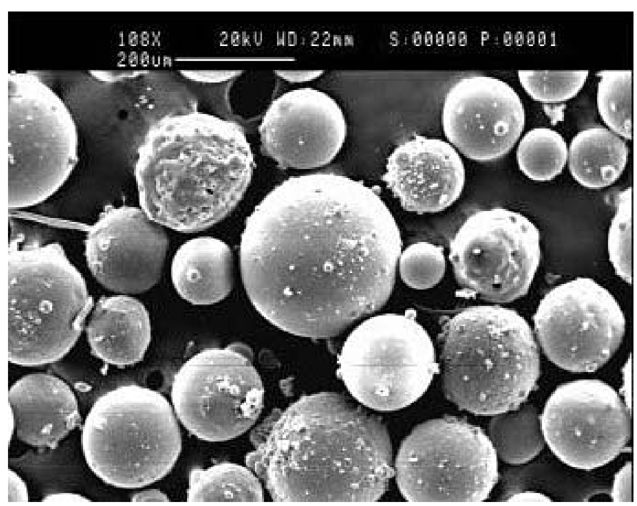


**Figure 1.** Hollow ceramic microspheres.

**Table 2.** Candidate lasers for laser-assisted thermal spray process

| Laser type | $CO_2$ | Nd:YAG: CW | Nd:YAG QS_pulsed | Fiber laser | Direct diode | Copper vapor |
|---|---|---|---|---|---|---|
| Average power | 1,000–20,000 W | 1,000–6,000 W | 5–100 W | 100–2,000 W | 100–4,000 W | 10–100 W |
| Peak/average | 1 | 1–2 | 1000–4000 | 1 | 1 | 1000 |
| Near field energy profile (raw beam) | Round mixed mode | Round top hat | Round gaussian | Round gauss, or round top hat | Rectangular top hat (soft) | Round top hat |
| $/watt | $50–150 | $120–200 | $1,000–4,000 | $200–1,000 | $70–120 | $2,000 |
| Typical peak | 3,000 W | 2,000 W | 200,000 W | 700 W | 4,000 W | 100,000 W |
| Power density | 3,000 W/mm$^2$ | 3,000 W/mm$^2$ | 10,000 W/mm$^2$ | 3,000 W/mm$^2$ | 1,000 W/mm$^2$ | 240,000 W/mm$^2$ |
| Pulse duration | CW | CW | 15 nanosec | CW | CW | 60 nanosec |
| Pulse frequency | CW | CW | 10,000 Hz | CW | CW | 10,000 Hz |
| Spot dimensions | 1.2 mm diam | 1.0 mm diam | 1.5 mm diam | 0.5 mm diam | 0.5 × 8 mm | 0.75 mm diam |
| Spot area | 1 mm$^2$ | 0.7 mm$^2$ | 1.7 mm$^2$ | 0.2 mm$^2$ | 4 mm$^2$ | 0.4 mm$^2$ |
| Overlap | 50% | 50% | 99.5% | 50% | 20% | 99% |
| Scan speed | 160 mm/sec | 160 mm/sec | 100mm/sec | 90 mm/sec | 20 mm/sec | |
| Coverage rate | 100 mm$^2$/sec | 66 mm$^2$/sec | 70 mm$^2$/sec | 22.5 mm$^2$/sec | 128 mm$^2$/sec | 40 mm$^2$/sec |
| Energy deposition | 30 J/mm$^2$ (3000 W ave) | 30 J/mm$^2$ (2000 W ave) | 0.4 J/mm$^2$ (30 W ave) | 31 J/mm$^2$ (700 W ave) | 31 J/mm$^2$ (4000 W ave) | 1.5 J/mm$^2$ (60 W ave) |
| Dwell rime | 16 msec | 12 msec | 0.003 msec | 11 msec | 25 msec | 0.006 msec |
| Asset cost | $200K | $300K | $175K | $175K | $300K | $150K |
| O&O cost | $150/h | $225/h | 130 $/h | $130/h | $225/h | $115/h |
| Coverage rate | 60 cm$^2$/min | 40 cm$^2$/min | 42 cm$^2$/min | 13.5 cm$^2$/ min | 77 cm$^2$/min | 24 cm$^2$/min |
| Cost/layer | $0.04 $/cm$^2$ | $0.09 $/cm$^2$ | $0.05 $/cm$^2$ | $0.16 $/cm$^2$ | $0.05 $/cm$^2$ | $0.08 $/cm$^2$ |

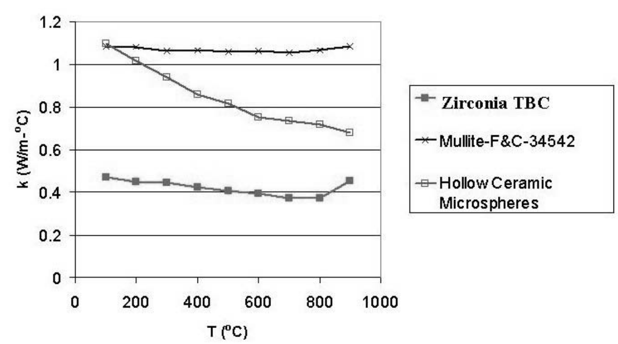


**Figure 2.** Thermal conductivity of a phosphate-bonded composite coating, consisting of hollow ceramic microspheres bound with aluminum phosphate binder, compared with the conductivity of zirconia and mullite thermal barrier coatings produced by plasma spraying.

Different techniques for applying the coatings have been explored. The consistency of the solution is adjusted using acidic water as thinner. Thick pastes and tapes of the material were deposited on substrates to form coatings. These coatings delaminated after thermal cycling to 650ºC. In order to enhance the contact area and apply more uniform coatings, thin slurries were applied with paint sprayers. Sprayed coatings with different filler-to-binder ratios were deposited on grit-blasted cast iron surfaces. A thin coating was first applied as a fine mist and allowed to dry for at least 5 minutes. This operation was repeated multiple times until the part was completely covered. Then a thickness of 2 mm was built up by depositing larger amounts in each step. Spraying produced the most aesthetic and thermal-shock-resistant coatings. A section of a coated cast iron diesel engine exhaust component is shown in Figure 3. After cycling three times to 650ºC, the coating did not crack or delaminate. Further coating deposition and characterization is in progress.

**Table 3.** Candidate lasers for tacking

| Laser type | $CO_2$ | Nd:YAG: CW | Nd:YAG: pulse pumped | Fiber laser | Direct diode |
|---|---|---|---|---|---|
| Average power | 1,000–20,000 W | 1,000–6,000 W | 100–1,000W | 100–2,000 W | 100–4,000 W |
| Peak/average | 1 | 1-2 | 2-10 | 1.5 | 1 |
| Near-field energy profile (raw beam) | Round mixed mode | Round top hat (fiber) | Gaussian (mirrors) | Round gauss, or round top hat | Rectangular top hat (soft) |
| $/watt | $50–150 | $120–200 | $200–300 | $200–1000 | $70–120 |
| Typical peak | 3,000 W | 2,000 W | 10,000W | 1,000 W | 4,000 W |
| Power density | 30,000 W/mm² | 30,000 W/mm² | 100,000 W/mm² | 30,000 W/mm² | 2500 W/mm² |
| Pulse duration | 0.2 msec` | 0.5 msec | 0.1 msec | 0.02 msec | 2 msec |
| Pulse frequency | 1,000 Hz | 400 Hz | 2,000 Hz | 10,000 Hz | 1,000 Hz |
| Duty cycle | 20% | 20% | 20% | 20% | 20% |
| Spot dimensions | 0.35 mm diam | 0.30 mm diam | 0.35 mm diam | 0.2 mm diam | 1.5 mm diam |
| Spot area | 0.10 mm² | 0.07 mm² | 0.10 mm² | 0.03 mm² | 1.6 mm² |
| % Coverage | 5% | 5% | 5% | 5% | 20% |
| Tack coverage | 100 mm²/sec | 28 mm²/sec | 200 mm²/sec | 300 mm²/sec | 1,600 mm²/sec |
| Coverage rate | 2000 mm²/sec | 560 mm²/sec | 4,000 mm²/sec | 6,000 mm²/sec | 8,000 mm²/sec |
| Energy deposition | 600 mJ/tack (3,000 W ave) | 1,000 mJ/tack (2,000 W ave) | 500 mJ/tack (1,000 W ave) | 70 mJ/tack (700 W ave) | 8,000 mJ/tack (4,000 W ave)o |
| Asset cost | $200k | $300k | $400k | $175k | $300k |
| O&O cost | $150/h | $225/h | $300/h | $130/h | $225/h |
| Coverage rate | 1200 cm²/min | 350 cm²/min | 1200 cm²/min | 1800 cm²/min | 2400 cm²/min |
| Cost/cm² | $0.002 $/cm² | $0.015 $/cm² | $0.004 $/cm² | $0.001 $/cm² | $0.001 $/cm² |

**Figure 3.** Cast iron manifold section with sprayed phosphate-bonded composite coating on outer diameter.

## Quasicrystalline Coatings

Quasicrystalline coatings have been produced using HVOF processing. The thermal conductivity of the coatings is under evaluation.

## Conclusions

1. Laser processing by "keyholing" critical coating areas has been selected for further evaluation based on the economics of this process. Laser-assisted thermal spraying will also be evaluated further in order to improve coating durability.

2. Phosphate-bonded composite coatings have shown promise in thermal cycling and will be further evaluated.

3. Quasicrystalline materials show a potential to have the coating strength properties of HVOF coatings, which will enhance their durability in TBC applications.

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## Presentations

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