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# Versatile Cold Spray (VCS)

**Prepared for:**

2020 R&D 100
Award Entry

LLNL-BR-812413

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# Versatile Cold Spray (VCS)

## 1. PRODUCT/SERVICES CATEGORIES

### A. Title

Versatile, Brittle Particle Cold Spray for Thermoelectrics and other Functional Materials

### B. Product Category

Process/Prototyping – Additive Manufacturing

## 2. R&D 100 PRODUCT/SERVICE DETAILS

### A. Primary submitting organization

Lawrence Livermore National Laboratory

### B. Co-developing organizations

TTEC Thermoelectric Technologies

### C. Product brand name

Versatile Cold Spray (VCS)

### D. Product Introduction

This product was introduced to the market between January 1, 2019, and March 31, 2020.
This product is not subject to regulatory approval.

### E. Price in U.S. Dollars

The first VCS production unit was fabricated and assembled at a cost of $50,000. The commercial price for a VCS unit would be approximately $35,000, a small fraction of the price for competitive additive manufacturing devices due to the technology's straightforward, streamlined, and portable design. VCS operating costs and energy demand are also low compared to competitors.

### F. Short description

Versatile Cold Spray (VCS) enables deposition of brittle materials, such as thermoelectrics, magnets, and insulators, while retaining their functional properties. Materials can be deposited on substrates or arbitrary shapes with no requirement to match compositions. The VCS system is low cost, easily portable, and easy to use.

### G. Type of institution represented

Government or independent lab/institute

### H. Submitter's relationship to product

Product developer

### I. Photos

Attached inline

### J. Video

https://youtu.be/inzxhgdEy2s

## 3. PRODUCT/SERVICE DESCRIPTION

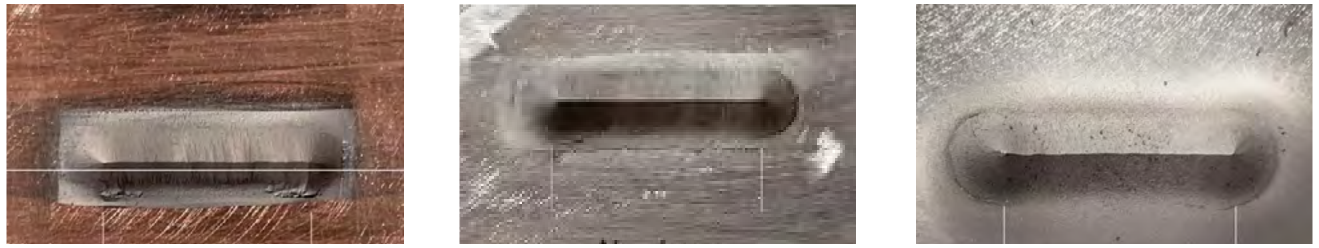
### A. What does the product/technology do?

Thirteen quadrillion British Thermal Units (BTUs) of energy are lost to waste heat each year from industrial operations across the United States. Based on Lawrence Livermore National Laboratory's energy use data for 2018 (https://www.llnl.gov/news/us-energy-use-rises-highest-level-ever), converting just half of the U. S. industrial waste heat into electricity would meet the country's total energy needs for nearly a month.

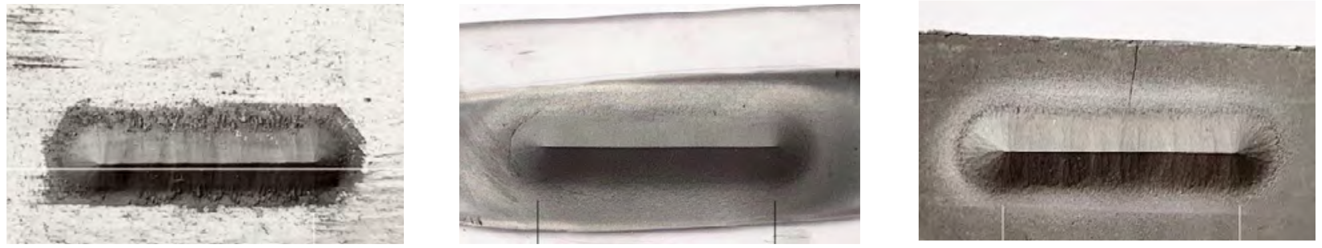
Applying thermoelectric material coatings to heat-emitting surfaces, such as cooling fins and transfer pipes in industrial facilities, would transform industrial components into thermoelectric generators that convert waste heat to electricity. Thermoelectric generators offer an elegant, energy harvesting option as they have no moving parts and do not rely on potentially toxic or flammable chemical reactions. However, until now, a reliable, cost-effective, and portable means of applying coatings to components of varying shapes and substrate materials, while retaining the coating's functional properties, has not been available.

**Versatile Cold Spray (VCS)**, developed through a partnership of Lawrence Livermore National Laboratory (Livermore) and industry partner TTEC, is a new cold spray technique that **deposits a broad range of brittle and glassy materials**, including functional materials such as thermoelectrics and magnets, onto **any substrate**. VCS **preserves the crystal structure of brittle materials**, unlike most competitive additive manufacturing techniques, so materials applied with VCS **maintain their functional properties**. This capability, combined with VCS's streamlined, portable design (Figure 1), opens the door to **creating thermoelectric generators and other functional components such as magnets and insulators** on industrial components with complicated form factors. Further, sequential deposition of different materials will allow the **complete additive manufacturing of complex devices** composed of combinations of metallic, semiconductor, magnetic, and thermal and electrical isolation materials.

*Figure 1 The streamlined VCS spray unit (left) and controller (center) are portable, enabling easy setup for coating of industrial components and materials (right).*



Copper Aluminum Stainless Steel



Aluminum Silicate Ceramic Glass/Quartz Syntactic Silicone Foam

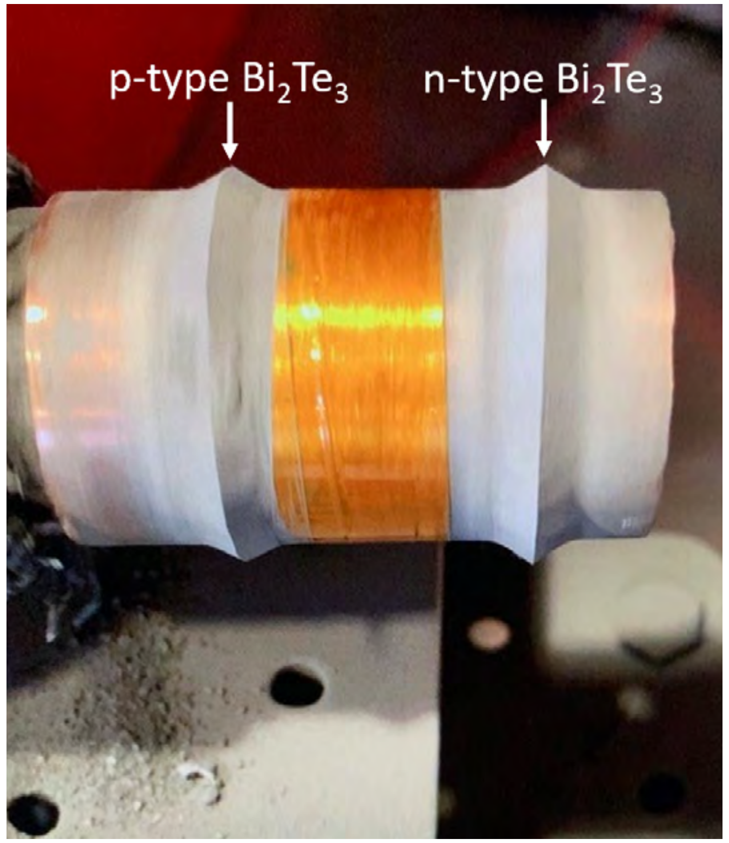
*Figure 2 VCS can coat a wide range of substrates, and has been successfully demonstrated on a number of common and unconventional substrate materials.*

### A More Versatile Additive Manufacturing Solution

Conventional cold spray has been used, primarily, to repair or patch ductile (malleable) materials by spraying micron-scale material powders delivered in a heated, high-pressure gas onto a substrate. "Cold" refers to the temperature of the gas, which is typically less than 500°C, below the material's melting point.

Conventional cold spray has been used successfully on steel, copper, chromium, and other ductile materials. However, with the exception of conventional cold spray's capability in adding corrosion-resistant coatings, the technology can only repair or patch materials rather than add functionality. When applied using conventional cold spray, the particles in brittle, functional materials such as semiconductors and magnets tend to shatter on impact rather than build a high-density deposit.

As described in more detail in the next section, **the innovative and patented VCS nozzle design and powder particle size distribution** enables the deposition of a broad range of brittle materials, driven by an embedding and interlocking process that achieves near-theoretical density while maintaining both mechanical and functional properties. Unlike many additive manufacturing techniques, particularly existing spray technologies, VCS can coat a wide variety of substrates, including non-planar surfaces. VCS has been demonstrated by the Livermore/TTEC team on metals, ceramics, glasses, and medium density organic foam materials. (Figure 2)



VCS can uniformly coat **complex shapes** such as the inside or outside of pipes. This feature, combined with VCS's portability, enables the technology to **apply coatings on equipment already installed** in industrial facilities, transforming fixed pieces of existing equipment into functional devices, depending on the coating selected. (Figure 3)

*Figure 3 VCS is capable of uniformly coating any shape component in place, such as the copper pipe pictured, and achieving >99% density. Thermoelectric coatings have been applied in this example.*

### Creating Functional Devices

VCS's capability to deposit brittle materials, on any shape or surface, in almost any location, opens the door to transforming components installed in industrial facilities into functional devices. As described in the next section, Livermore and TTEC have demonstrated VCS's ability to deposit thermoelectric materials to create thermoelectric generators on complex shapes, enabling their fabrication on, for example, hot transfer pipes, heat-generating operating equipment such as electric motors and internal combustion engines, and nuclear waste containers.

The Livermore/TTEC research team has also demonstrated VCS's effectiveness in depositing several classes of magnetic materials used for motors or generators as well as insulators serving as a protective layer in other devices. **VCS's success in depositing thermoelectric and magnetic materials without significant loss of function indicates the technology is capable of depositing other functional materials with similar density and ductility, creating other devices for energy generation and storage**.

### B. How does the product/technology work?

In cold spray technologies, high-pressure gas is heated, accelerating the gas to supersonic speeds between Mach 2 and Mach 4. Micron-scale particles are injected into the gas stream and directed onto a substrate by a nozzle. In conventional cold spray, material particles exiting the nozzle plastically deform (permanently change shape) and experience adiabatic shear stress, causing them to consolidate into a high-density deposit. Ductile materials are suited to conventional cold spray because they can plastically deform. As noted earlier, conventional cold spray technology is not capable of depositing materials composed solely of non-ductile or brittle materials; brittle material particles larger than 10 microns either shatter and disperse on impact or sandblast the deposition surface.

The **key differences** for VCS are its **innovative nozzle design** and the use of a **feedstock with tailored size distribution**. This results in particle impact velocities well below those typically required for ductile material deposition. A schematic of the system is shown in Figure 4, along with multiphysics modelling of gas velocity used to inform and refine nozzle geometry and powder injection processes. The VCS design creates localized pressure gradients directly above the

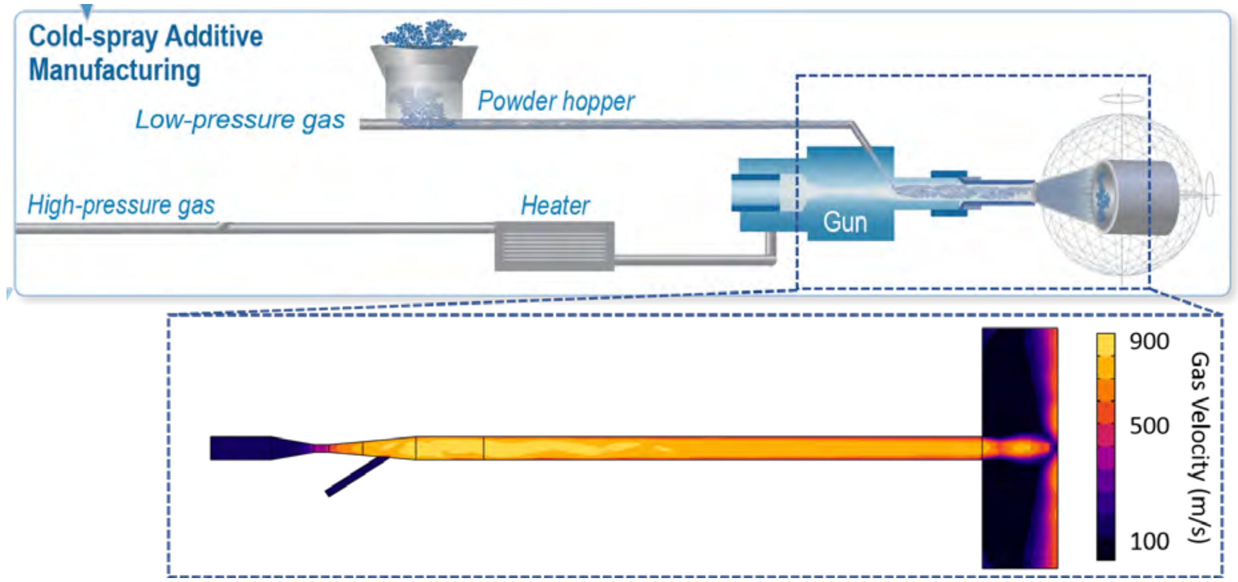


*Figure 4 VCS injects micron-scale materials downstream of an innovative nozzle (top image) as indicated in the computer simulation (bottom image), The result is gas/particle flow at a supersonic, uniform speed at the nozzle exit slowing just short of the surface to be coated. The gas/particle mixture then conforms to the surface rather than deflect at right angles.*

substrate, enhancing deposition efficiency and preventing particles being swept away by the high pressure gas.

As a result, **deposited materials embed and interlock** on the surface, rather than deform, which preserves the tailored microstructure that drives their unique, functional properties. Follow-on coating further densifies previously-coated layers. Careful control of feedstock size enhances the ability of particles to consolidate without the material shattering or becoming damaged.

VCS's nozzle design and powder preparation strategy enable a far greater range of materials to be deposited without matching materials to substrates and without the need for ductile materials to act as adhesives. Surface irregularities at that scale act as attachment points, and the highly irregular shape of the brittle particles allow the mix of particle sizes to hold together and densify on subsequent impacts. In addition, both the nozzle design plus the downstream addition of the particles allows highly-cohesive powder materials to be drawn into the nozzle without clogging. The patented process enables the addition of additives to aid the flow of cohesive powders into the supersonic gas stream, if required, without changing the composition of the deposited functional material.

## Streamlined, Portable System

The system as deployed consists only of a spray unit and its controller, making VCS **portable and easy to set up**. VCS could easily be integrated into any production setting as well. For example, the spray unit could be mounted on a robotic arm to generate very complex shapes.

The technology's capital cost is low due to the simplicity of design, and power demands are low. Operating costs are also low as VCS works with nitrogen rather than expensive helium, which is preferred for high-pressure cold spray.

## Creating Thermoelectric Generators

Thermoelectric materials such as bismuth telluride combine high electrical conductivity and low thermal conductivity and generate a voltage in response to temperature gradients. In other words, thermoelectric materials applied to heat-emitting devices or parts can harvest waste heat and convert it to electricity.

The Livermore/TTEC team created a prototype thermoelectric generator with parallel p- and n-type bismuth telluride electrodes by using VCS to coat the outer surface of a copper pipe with bismuth telluride. (Figure 5) The sprayed material achieved greater than 99% density and was largely free from pores.

Compared to a prototype in which bulk bismuth telluride was simply adhered to a pipe using conductive epoxy, the current output for the VCS-coated pipe increased dramatically at high temperatures. (Figure 6) These results point towards VCS's ability to maintain functional qualities of a coating material. In addition,

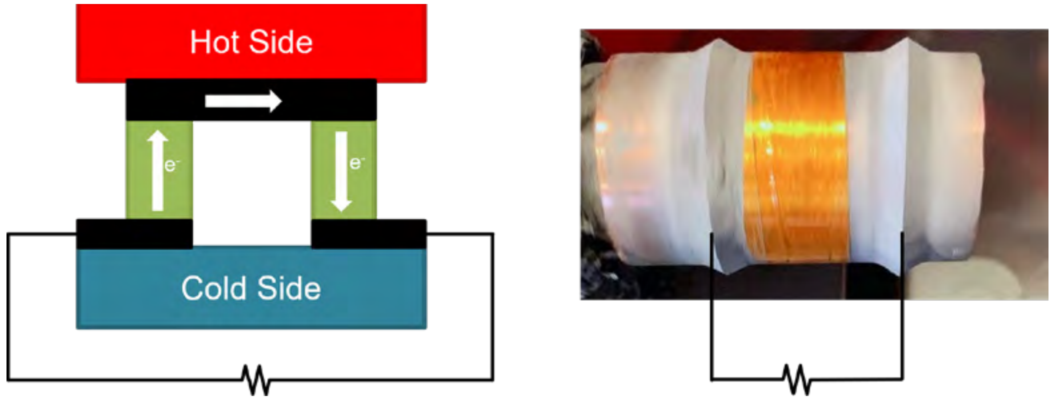


*Figure 5 Thermoelectric materials harvest waste heat and convert it to an electric current (left). Coating a transfer pipe or other heat-emitting component with p- and n-type thermoelectric electrodes creates a thermoelectric generator (right).*

VCS's ability to coat without using binders ensures excellent mechanical and thermal contact between the coated surface and thermoelectric material and good electrical contact at the electrodes.

**VCS offers the capability to use a wide variety of thermoelectric materials that can be tailored to thermal conditions at the waste heat source** from materials with good thermoelectric properties, at or below 230˚C, to high temperature materials with good thermoelectric properties at 500˚C or higher. In addition, VCS's unique material deposition aspects enable formation of shaped thermocouple elements, layered thermoelectric material elements, and nanomaterial-doped thermoelectric material elements. Capabilities for large-area deposition capability and micro-thin thermoelectric materials open up a much broader range application space for these solid state energy recovery systems.

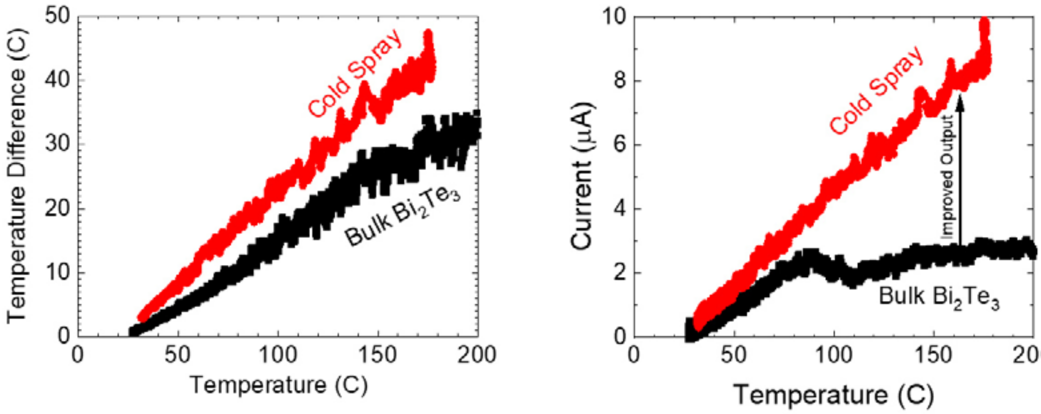


*Figure 6 Comparing the performance of the thermoelectric generator created using VCS (red data points) and bulk material adhered to a pipe (black data points). The materials maintain a similar temperature gradient between hot and cold sides (left), but the cold sprayed material outperforms the bulk application at higher temperatures (right), due to a combination of enhanced Seebeck voltage and improved thermal contact with the hot pipe.*

## C. Product Comparison

As indicated in Table 1, VCS's competitors include other cold spray and additive manufacturing technologies. Only VCS offers the capabilities and strengths of other technologies in a low cost, streamlined, portable device capable of cost-effectively creating thermoelectric generators for use in industrial facilities. VCS, therefore, offers the potential for a major expansion in the cold spray deposition technology application space with its many advantages over other coating/material deposition methods.

**VCS coats both ductile and brittle materials and retains material functional properties**. As noted earlier, conventional cold spray is limited to ductile metals because brittle, functional materials shatter in almost all cases when delivered in the conventional approach. Materials deposited by plasma spray, a close cousin of cold spray, often require extensive post-processing to recover functional properties. High-energy additive manufacturing technologies such as direct metal write (DMW) and laser powder bed fusion (LPBF) destroy crystal structure and, therefore, functional attributes. Low-energy additive manufacturing technologies such as direct ink write (DIW) have performance limits due to low material density and require extensive post-processing to remove inks and binders. In embodiments where the ink is not removed, such as bonded magnet processing, the melting point of the ink itself can limit a material's service temperature. **VCS is a rare technology that can deposit on surfaces irrespective of geometry or composition**, further demonstrating its versatility.

Due to the high kinetic energy accessed during deposition, **VCS can coat complicated surfaces and shapes for in-place fabrication** of devices such as thermoelectric generators on pipes or valves and permanent magnets inside motor housings or generator parts. Additive manufacturing techniques such as LPBF cannot approach this high level of versatility and portability. **VCS is the only technology that can be used in all three noted applications: energy harvesting, magnetic materials, and electrical and thermal insulators**. Further, it is capable of combining these materials through sequential deposition, for example, to create layered thermoelectric generators or laminated magnetic structures.

Comparing cost and ease of operation, VCS outranks almost all competitors with its low capital, operating, and energy costs combined with a small size and easy portability. While low pressure cold spray and DIW match VCS in operational considerations, they fall short in their performance across multiple materials, installations, and applications.

## D. Comparison summary

| | **SPRAY TECHNIQUES** | | | | **ADDITIVE MANUFACTURING TECHNIQUES** | | |
|---|---|---|---|---|---|---|---|
| **CHARACTERISTICS** | **LLNL/TTEC VERSATILE COLD SPRAY** | **High Pressure Cold Spray** | **Low Pressure Cold Spray** | **Plasma spray** | **Laser Powder Bed Fusion** | **Direct Ink Write** | **Direct Metal Write** |
| Coats complex shapes and surfaces | 🟩 | 🟩 | 🟩 | 🟩 | 🟥 | 🟥 | 🟥 |
| Capable of depositing brittle functional materials | 🟩 X Bi2Te3, Nd2Fe14B, (Mn,Zn)-Ferrite, Tetrahedrite, Borosilicate glass | 🟥 | 🟥 | 🟩 | 🟩 Nd2Fe14B | 🟩 Nd2Fe14B | 🟥 |
| Retains properties of all functional material classes | 🟩 | 🟥 | 🟥 | 🟥 | 🟨 | 🟩 | 🟥 |
| Achieves deposition density (>99%) for required strength and function | 🟨 | 🟩 | 🟥 | 🟩 | 🟩 | 🟥 | 🟩 |
| Can deposit on dissimilar substrates, e.g., metal-ceramic bonding | 🟩 | 🟨 | 🟨 | 🟥 | 🟥 | 🟩 | 🟩 |
| Feedstock sizes, characteristics | 🟩 0.1 – 10 microns | 🟨 5 – 100 microns | 🟨 10 – 80 microns, flowable | 🟩 5 – 100 microns, wires | 🟥 Flowable, spreadable | 🟨 Must be miscible with inks | 🟩 No limitations |
| **APPLICATIONS** | | | | | | | |
| Energy Harvesting: Thermoelectrics or piezoelectrics | 🟩 | 🟥 | 🟥 | 🟩 | 🟥 | 🟩 | 🟥 |
| Magnetic Materials: Permanent magnets for use in motors and generators | 🟩 | 🟨 with binder | 🟥 | 🟥 | 🟩 | 🟨 with binder | 🟥 |
| Electrical and Thermal Insulators: Cladding or protective layers in other devices | 🟩 | 🟥 | 🟥 | 🟩 | 🟩 | 🟩 | 🟥 |
| **OPERATION** | | | | | | | |
| Capital / Operating Costs | 🟩 $ / $ | 🟥 $$$ / $$ | 🟩 $ / $ | 🟥 $$$ / $$ | 🟥 $$$$ / $$ | 🟩 $$ / $ | 🟥 $$$ / $$ |
| Energy requirements | 🟩 Low | 🟨 Medium | 🟩 Low | 🟥 High | 🟥 High | 🟩 Low | 🟥 High |
| Portability / Easy Setup | 🟩 Easy Setup | 🟨 Somewhat Easy Setup | 🟩 Easy Setup | 🟥 Difficult Setup | 🟥 Difficult Setup | 🟩 Easy Setup | 🟥 Difficult Setup |
| Footprint | 🟩 Small | 🟨 Medium | 🟩 Small | 🟨 Medium | 🟥 Large | 🟩 Small | 🟥 Large |

*Table 1: Comparison of VCS with other spray techniques and additive manufacturing technologies. Green indicates the technology meets the performance characteristic, and red indicates the technology does not. Yellow indicates limited or situational performance.*

### E. Limitations

A current limitation of VCS is the occasional requirement for a post-deposition anneal to remove defects introduced during the spray process, a step that may not be practical for some applications. The Livermore/TTEC team is addressing this limitation by developing custom formulations of thermoelectric or magnetic materials specifically designed for spraying. This tight integration of feedstock optimization and deposition conditions is a paradigm gaining traction in the wider additive manufacturing community. In addition, ongoing research seeks to improve deposition efficiency by tuning powder size and gas velocity. However, non-adhering powder can be re-collected and resprayed in the current design.

The mechanism of adhesion and buildup in traditional cold spray deposition is understood to be related to adiabatic shear stress and plastic deformation of the particles, but these processes are not applicable to the brittle powders VCS can deposit. Without a general theory of cold spray applicable to these materials, optimization of spray conditions is required for every new material that is used. However, as the library of studied materials grows, researchers will be able to adapt to new additions more easily. Developing a more complete model of the deposition and buildup process is an ongoing project of the VCS team. Recent research and development efforts so far have indicated that a specific particle size distribution has applicability to a wide range of brittle materials spanning a MOHS hardness range from 2.5 to 8.0, and that the critical velocity at impact required for brittle materials may be held within a much narrower range of gas temperature and gas pressure conditions.

## 4. SUMMARY

Versatile Cold Spray (VCS) outperforms other cold spray and additive manufacturing techniques by depositing both ductile and brittle materials to any substrate of any shape without adhesives. The unique VCS nozzle and feed system preserves the functional qualities of brittle materials such as semiconductors, including thermoelectrics, and magnets, achieving a coating with greater than 99% density. The streamlined, portable, low-cost VCS design enables high-density, functional coatings in place, providing a viable pathway to creating energy-harvesting thermoelectric generators from heat-emitting industrial components of any form factor. These thermoelectric generators present an elegant solution—with no moving parts or chemicals—to begin to capture the 13 quadrillion BTUs of energy lost to waste heat each year from U. S. industrial operations. The Livermore/TTEC team that developed VCS has demonstrated its effectiveness in building a thermoelectric generator as well as its capability to apply magnetic coatings, creating permanent magnets inside motor housing or generator parts, and insulating materials, an important component of energy harvesting and storage devices.

## 5. CONTACT INFORMATION

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## 6. AFFIRMATION

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## 7. REFERENCES

There are no references for this entry.

## 8. ATTACHMENTS

Letters of Support (separate files)
- David Beckwith, Powdertech
- Aaron Nardi, U. S. Army Research Labs
- Donald Morelli, Michigan State University
- Joseph Farmer, LLNL Directorate Senior Scientist (retired)

User Manual: TTEC Versatile Cold Spray System Model 1970