Thermal Spray and Laser Applied TCHP Barrier Coatings for Extended Life

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Abstract

TCHP is a growing new family of innovative materials that provide advanced wear resistant solutions for critical wear components. Previously, TCHP powders had been pressed & sintered into solid shapes, such as wire drawing dies and cutting tools, and now TCHP has been successfully deposited as surface coatings by HVOF thermal spray and laser-based deposition processes.

Allomet Corporation created this novel family of industrial metal powders called Tough Coated Hard Powders (TCHP), or EternAloy®. These high performance metallurgical powders consist of extremely hard "core" refractory particles that are then CVD coated with nanolayers of WC and Co binder, for example. Each particle is encapsulated in a tough WC-Co outer "shell" that surrounds a wear-resistant core (e.g., Al_2O_3). When sintered or applied using thermal spray methods, the tough outer layers chemically bond in the sintered or deposited coating, combining high strength, heat resistance, and toughness of cemented carbides with the chemical and abrasion wear resistance of harder core particles.

Thermally applied alumina core particle TCHP offers high microhardness (1400 HV_{300}) and bond strengths over 70 MPa, depending on the HVOF spray parameters. Deposited microstructures show a very uniform distribution of alumina particles in the tungsten-carbide cobalt matrix with porosity of less than 0.5%, over a wide range of spray parameters. In fact, thermally sprayed TCHP microstructures are highly uniform and appear quite similar to pressed and sintered microstructures.

TCHP surface coatings have also been deposited utilizing two different laser-based techniques. Using the same alumina core particle TCHP powder, even higher microhardness (2000-2400 HV1) has been measured which we believe will show excellent abrasion resistance. Initial positive results are leading to further development of laser deposited TCHP materials as wear resistant coatings.

Together with experts in the surface coating industry, Allomet is further advancing this new class of materials to create superior coatings to prolong the operational life of critical wear parts. These partnerships, combined with Allomet's nanotechnology and product development capabilities, set a path toward providing long-term solutions for TCHP to be considered as a surface coating material solution for significantly improving wear resistance.

Keywords

TCHP, Wear Resistant Coatings, HVOF, Thermal Spray, Encapsulated Particles, Laser Metal Deposition, WC-Co Coatings

Introduction

Tough Coated Hard Powders

Tough Coated Hard Powders (TCHPs) are a new family of patented, high performance metallurgical powders that incorporate unprecedented combinations of property extremes. They represent a class of engineered microstructure P/M-based hardmetals having combinations of critical properties that improve performance and productivity. These engineered property combinations include toughness, abrasive and chemical wear resistance, low coefficient of friction, and light weight…at levels not previously seen. TCHP powders can be fabricated into a multitude of industrial metal-cutting and wear parts while leveraging their key attributes to improve manufacturing productivity.

These TCHP powders are created by incorporating hard particles in a tough matrix using proprietary manufacturing technologies. Engineered nanostructures are created by encapsulating extremely hard "core" particles with a tough outer layer(s), for example tungsten carbide and cobalt, which in the consolidation process become a contiguous matrix. TCHP powders and consolidated die blanks are manufactured and sold by Allomet Corporation (North Huntingdon, PA) as EternAloy®. The processing, structure and properties of TCHP have been described in previous publications [1, 2]. Representative "core" particles include those traditionally used for extreme wear resistance [e.g., diamond, cBN, Ti(C,N), TiN, Al_2O_3, …].

One typical TCHP material utilizing alumina (Al_2O_3) as the core particle has shown to be highly resistant to abrasive wear and is especially suited to wire draw dies and similar applications. Example microstructures of an alumina TCHP grade are shown in Figure 1. Another recently developed EternAloy® material utilizes titanium carbonitride Ti(C,N) core particles to provide higher thermal conductivity along with high hardness in a tungsten carbide and cobalt matrix. Microstructural photos of this material are shown in Figure 2. The Ti(C,N) TCHP grade is beginning to demonstrate significant performance advantages over the alumina TCHP in high speed wire drawing where high heat generation at the die-wire interface rapidly wears WC-Co dies. Allomet continues to develop additional TCHP grades as this group of new materials expands to meet performance demands of more applications.

(a) (b)

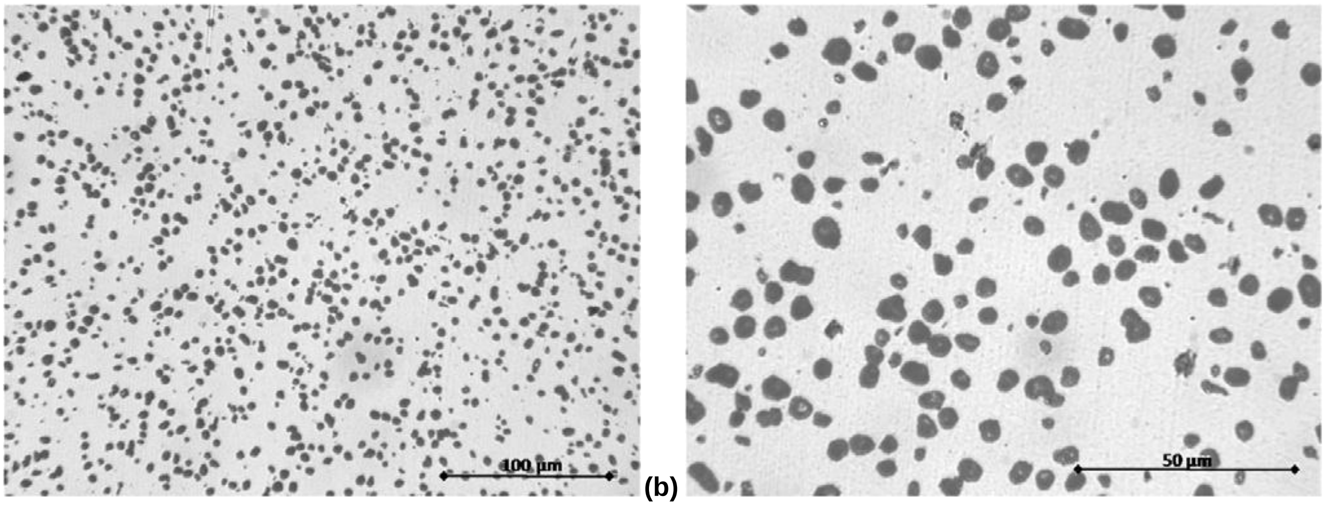


Figure 1: SEM photos, collected in backscattered electron mode (BSE), of the alumina TCHP consolidated microstructure. The dark circular areas in the microstructure are the hard, alumina core particles and the bright regions illustrate the WC and Co matrix. **(a)** 200X and **(b)** 500X magnifications.

(a) (b)

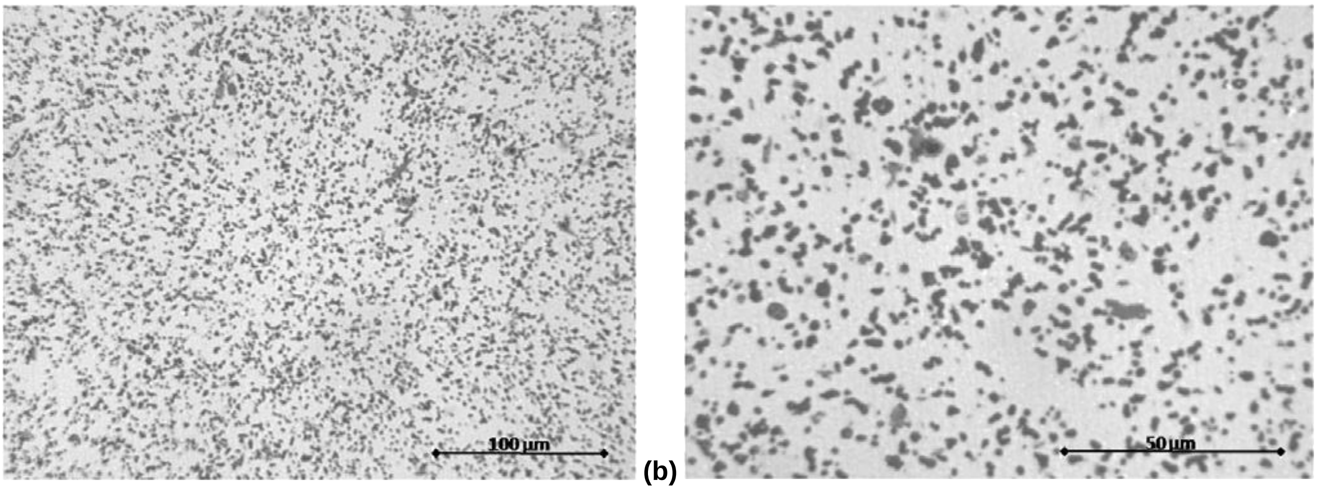


Figure 2: SEM photos, collected in backscattered electron mode (BSE), of the Ti(C,N) TCHP consolidated microstructure. The dark areas in the microstructure are the hard, Ti(C,N) core particles and the bright regions illustrate the WC and Co matrix. **(a)** 200X and **(b)** 500X magnifications.

Applications for TCHP Coatings

Applications for TCHP coatings include those in oil and gas, machine tools and industrial manufacturing industries where extreme wear resistance is required. Many types and combinations of wear mechanisms are observed in these applications. TCHP has been shown to perform extremely well in sliding wear applications, in particular. For example, customers using TCHP grade TL-3 wire drawing dies benefit from 7X and greater increases in die life compared to conventional carbide dies in drawing high strength steel tire cord [1, 2]. Applications also include those where a combination of hardness and toughness is required. For example, conventional materials are typically either hard or tough. As depicted in Figure 3, Allomet's EternAloy® TCHP technology provides a new class of materials, creating options previously unavailable to metallurgists and design engineers, and thus addressing a historical engineering challenge of trading off one property for another.

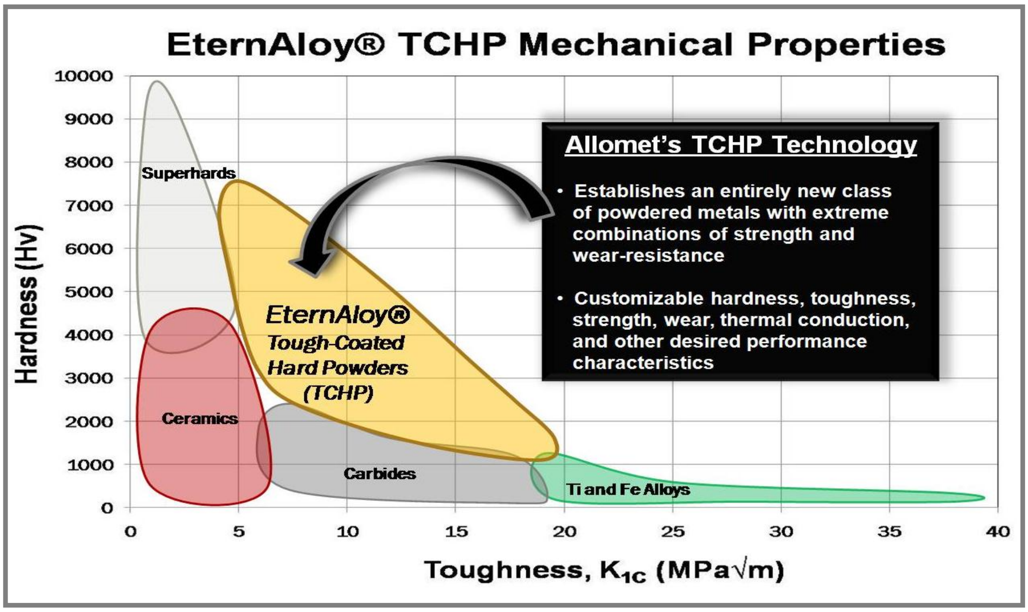


Figure 3: EternAloy® TCHP Mechanical Properties.

Testing Overview

Development of Thermally Applied TCHP Coatings

Allomet TCHP surface coatings have been generated using a variety of thermal spray and LMD equipment, including Sulzer-Metco HVOF thermal spray, Praxair HVOF and Plasma thermal spray, and Trumpf and SPI Laser deposition systems. Collaborations have been made through partnerships with both thermal spray coating and laser metal deposition suppliers, the purpose of which was to develop TCHP coatings, and thus, to expand industrial applications of TCHP.

During the HVOF coating development process, a number of spray parameters were varied, including oxygen:fuel ratio, total gas flow, combustion pressure, feed rate, and spray distance. This initial testing phase has revealed the opportunity for “tuning” the thermal spray process parameters to achieve various microstructures and, consequently, performance. For example, parameters have been adjusted to achieve high hardness and wear resistance as well as to achieve increased thickness and toughness. Information on both systems is presented in this document. The former system is referred to as Parameter Set A, and the latter is Parameter Set B.

Allomet TCHP surface coatings have been deposited with Laser Metal Deposition (LMD) utilizing two different techniques. One technique uses TCHP only, the results of which are presented in this document. A Nd:YAG laser was used for macro LMD, and a fiber laser was used for micro LMD. LMD parameters, such as laser power, velocity, powder feed rate, and laser beam diameter, were varied to achieve a low dilution value. A second technique allows for TCHP to be mixed with a metal matrix alloy. Results using this approach are currently being evaluated.

Initial Measurements and Results

<u>HVOF</u>

HVOF thermal spray of TCHP material has produced bond strengths ranging from 9,000 psi (62 MPa) to over 12,000 psi (83 MPa) and microhardness values ranging between 900 and 1400 HV_{300}, both depending on the TCHP grade and spray parameters. The microstructures show a uniform distribution of core particles in the tungsten-carbide cobalt matrix with porosity values at less than 1% for a range of spray parameters. In addition, the similarities between the as-sprayed microstructures and the sintered microstructures prepared for TCHP solid parts in wire applications indicate high potential for superior wear resistance. A “build-up” test shows that Allomet TCHP material can be sprayed to thicknesses exceeding 0.060” (1.5 mm) with no crack formation, as determined using dye penetrant. This is twice the thickness that is typically achieved with conventional carbide HVOF coatings.

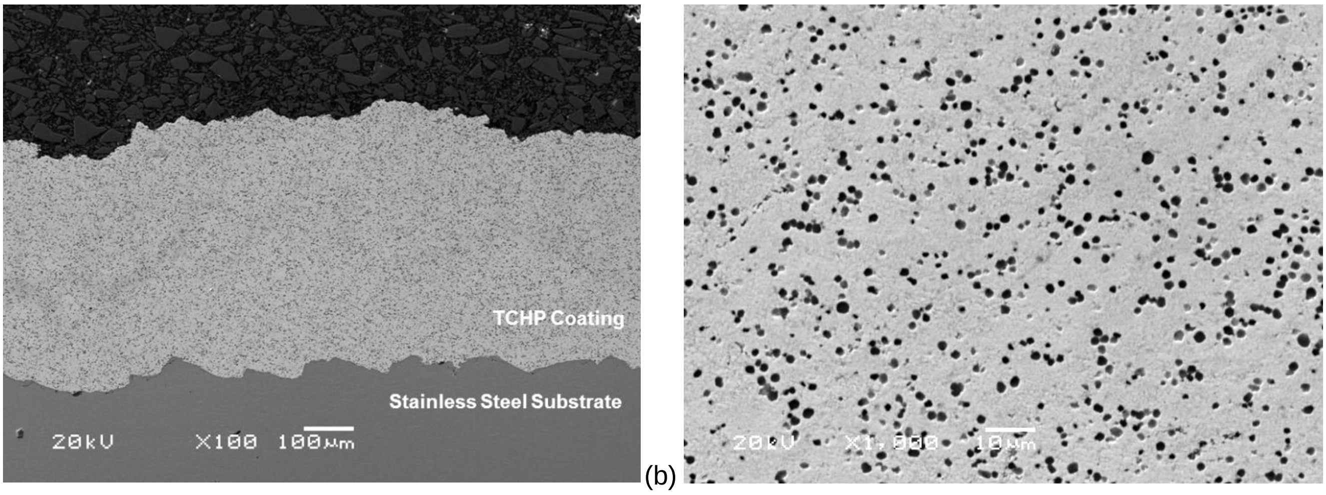
<u>LMD</u>

LMD using only TCHP has produced average microhardness values ranging from 1500 HV1 to 1950 HV1 and peak values ranging from 1750 HV1 to 2570 HV1, depending on the deposition parameters. The LMD microstructures show acceptable dilution values of less than 20% and strong metallurgical bonding to the substrate. Also, a standard pin-on-disc test shows no measurable abrasion after 2000 meters. Preliminary results of LMD using TCHP mixed with a metal matrix alloy result in a multi-phase microstructure, the potential performance benefits of which are being determined. This technique allows for various combinations of materials for targeting specific performance requirements. For example, by mixing TCHP with a metal matrix alloy, one has the ability to provide additional strength and ductility to a TCHP-only LMD coating. The initial positive results obtained using LMD have strongly indicated that more vigorous evaluation and further development is desirable in order to expand the full potential of laser deposited TCHP material as wear resistant coatings.

Test Results

HVOF Thermal Spray of Allomet TCHP

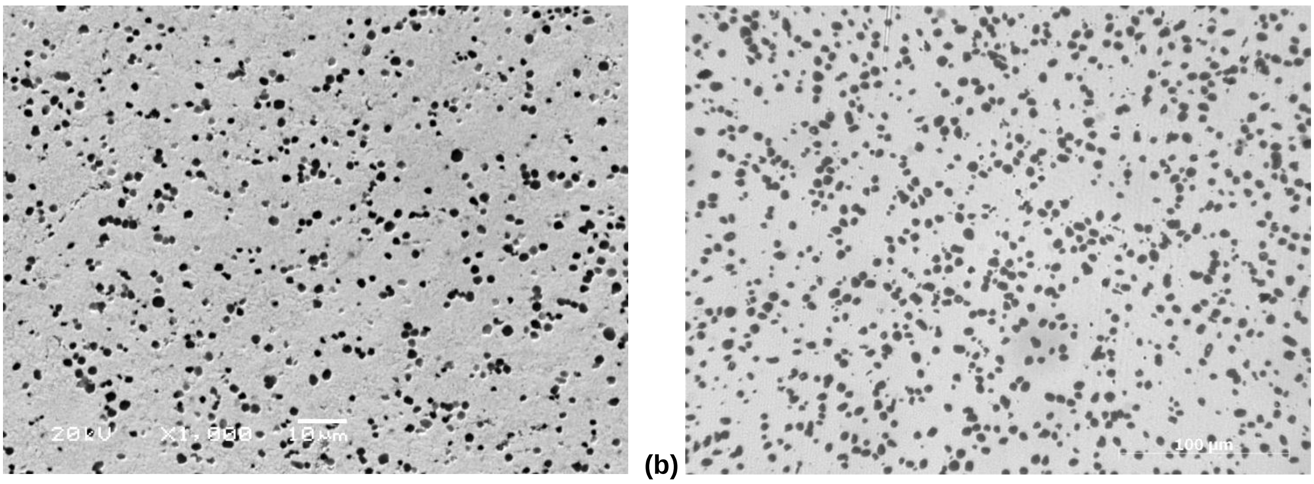
Allomet TCHP grade NL-3 material has been thermally sprayed by a variety of industrial and academic partners using three thermal spray gun manufacturers, including Sulzer-Metco and Praxair. Similar microstructures have been obtained by each organization and set-up. A typical microstructure is shown in Figure 4.



(a) (b)

Figure 4. Allomet TCHP NL-3 (Al_2O_3 core particles, encapsulated with WC-Co) HVOF Thermally Sprayed Coating on a stainless steel substrate. Alumina particles appear as the black areas and are incorporated into the WC-Co matrix. **(a)** 100X and **(b)** 1000X magnifications.

The thermally sprayed microstructure is very similar to a typical sintered TCHP microstructure, indicating high potential for superior wear resistance and improved mechanical properties as observed in wire drawing applications. Examples of both microstructures are provided in Figure 5.



(a) **(b)**

Figure 5. **(a)** Allomet TCHP NL-3, (Al_2O_3 core particles, encapsulated with WC-Co) HVOF Thermally Sprayed Coating, **(b)** Allomet TCHP NL-3, Pressed and Sintered Microstructure.

By using Parameter Set B spray conditions, a coating thickness of 0.062” (1.6 mm) was achieved with no cracks as tested by a dye penetrant. This “build-up” test shows the flexibility of the TCHP material, when applied to industrial applications, to allow for overlap without the risk of cracking or delamination while maintaining sufficiently high wear resistance. In addition, the build-up amount is twice the thickness that is typically achieved with using commercial WC-Co HVOF powders.

Sample coupons of TCHP Parameter Set A and B were cross-sectioned and prepared for metallographic analysis and hardness determination. Figure 6 presents SEM photomicrographs at low and high magnification of Parameter Set A. The TCHP microstructures show a uniform distribution of alumina particles in the tungsten carbide-cobalt matrix. The sample shown in Figure 7 is a cross-section of the build-up test sprayed with Parameter Set B. These TCHP microstructures show that a uniform microstructure is maintained as the thickness increases. Specific porosity data was not collected; however, a visual inspection estimates porosity values at less than 1% and perhaps even approaching 0.5%. This value is based on porosity measurements obtained on initial TCHP coatings.

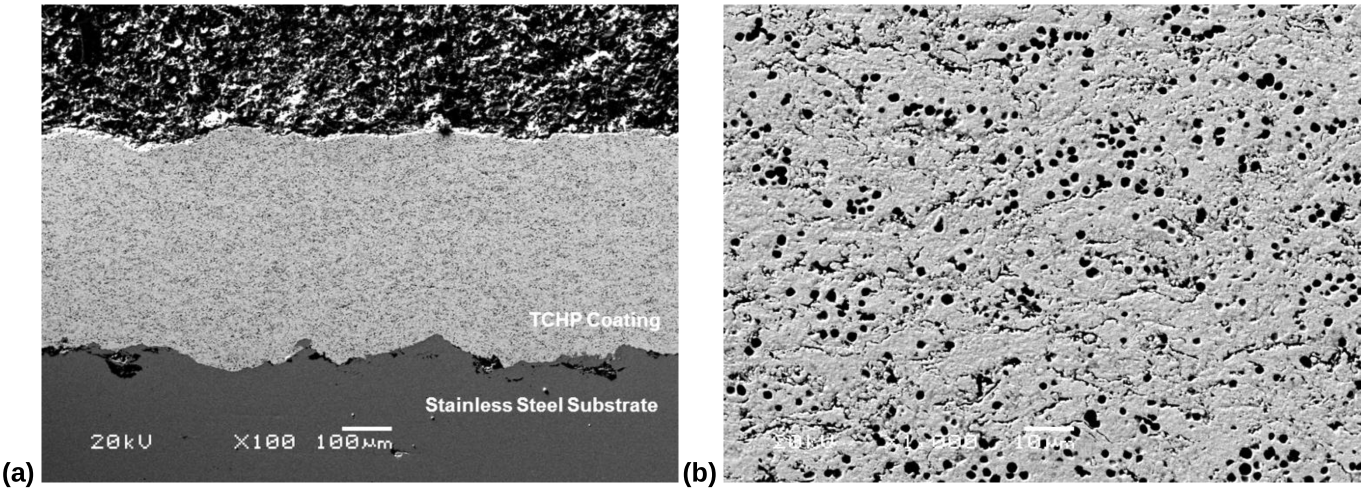


Figure 6. Parameter Set A – HVOF - applied Allomet TCHP NL-3-2 on a stainless steel substrate. **(a)** 100X and **(b)** 1000X magnifications.

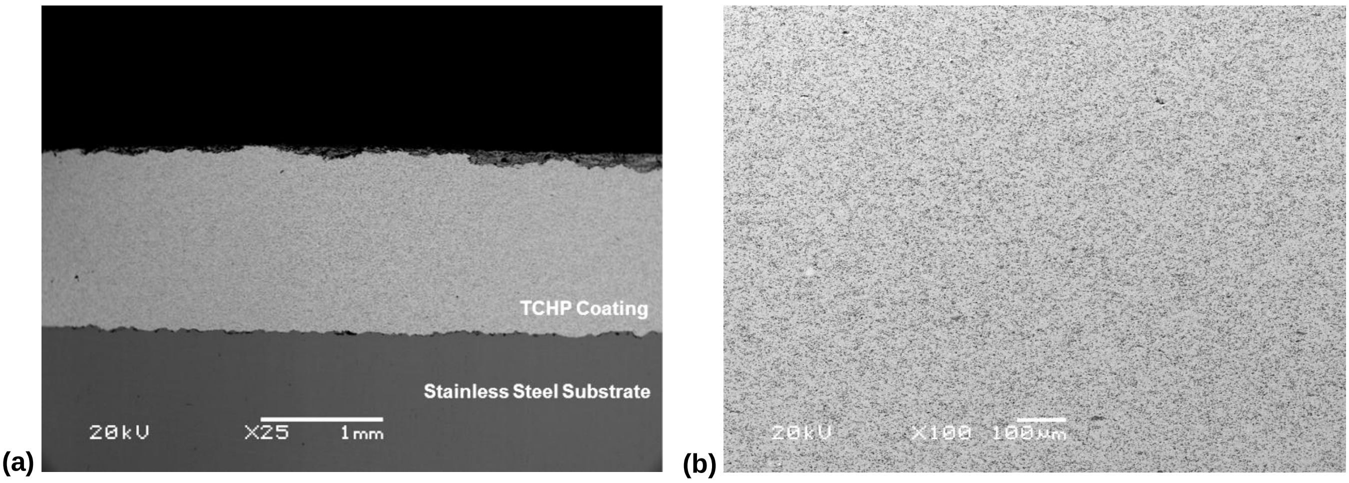


Figure 7. Parameter Set B – HVOF - applied Allomet TCHP NL-3-2 Build-up Sample on a stainless steel substrate. No cracking is observed throughout the entire 0.062” (1.6 mm) thick coating. **(a)** 25X and **(b)** 100X magnifications.

Microhardness measurements were performed by RJ Lee Group, Inc. using a Buehler 1600-6306 hardness tester and Vickers diamond indentor. Figures 8 and 9 show the microhardness values obtained at measured distances from the substrate for Parameter Sets A and B, respectively. Spray Parameter Set A provides hardness values ranging from 1070 to 1324 HV_{300}. Microhardness measurements obtained on the Parameter Set B build-up sample ranged from 866 to 1124 HV_{300}.

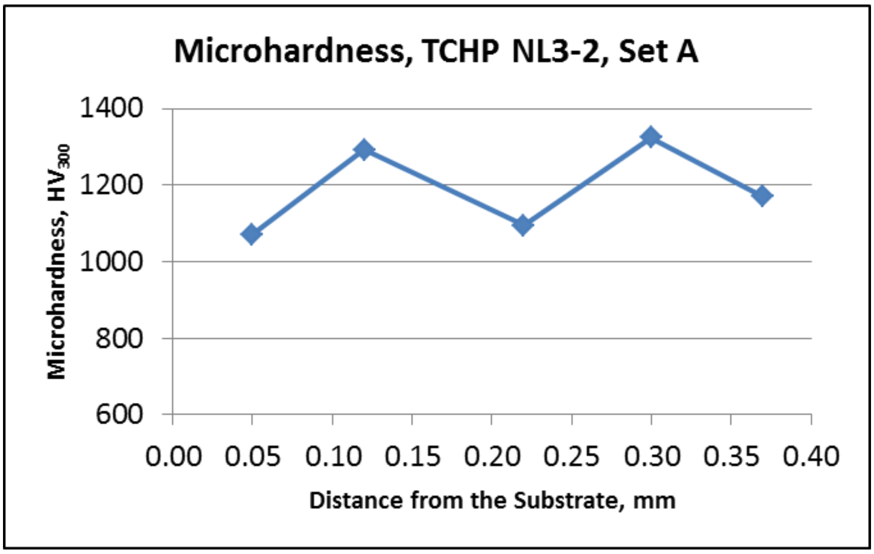


Figure 8: Microhardness of HVOF – applied Allomet TCHP NL-3-2: Parameter Set A.

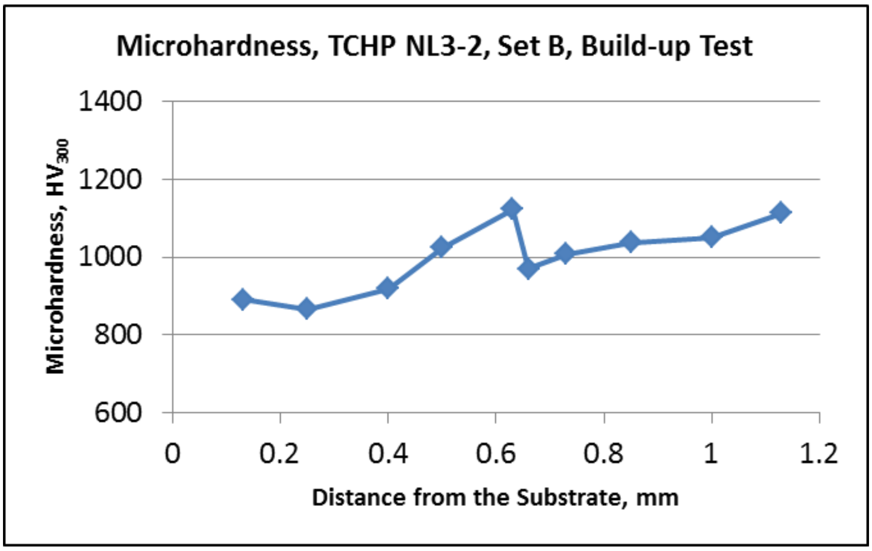


Figure 9: Microhardness of HVOF – applied Allomet TCHP NL-3-2: Parameter Set B, Build-up Test.

Allomet TCHP grade TL-3 material has been thermally sprayed with a Praxair JP-8000 HVOF system. The following results were measured by a partner thermal spray coating supplier. A typical HVOF TL-3 microstructure is given in Figure 10. Microstructure evaluation shows less than 1% porosity and less than 3% interface contamination with no cracks or delaminations. Microhardness values range from

1190 to 1392 HV_{300}, with an average value of 1308 HV_{300}. Superficial hardness values range from 94.0 HR-15N (86.5 HRA) to 94.9 HR-15N (88.0 HRA), with an average value of 94.3 HR-15N (87.0 HRA) and a standard deviation of 0.3 HR-15N. This relatively low standard deviation indicates a highly uniform microstructure.

Figure 10. Allomet TCHP TL-3 (Ti(C,N) core particles, encapsulated with WC-Co) HVOF Thermally Sprayed Coating on a 410 stainless steel substrate. Ti(C,N) particles appear as the black areas and are incorporated into the WC-Co matrix. (Photo courtesy of Hayden Corporation, West Springfield, Massachusetts, USA)

Laser Metal Deposition (LMD) of Allomet TCHP

LMD coatings have been produced using Allomet TCHP grade NL-3 material. Parameters were varied to obtain a typical Dilution of less than 20%. Figure 11 shows a cross-section of a single LMD layer with a Dilution value of 17%. Dilution is defined as the amount of intermixing of the clad and substrate materials. A low dilution value is desired to maintain the properties of the clad material and the possibility of avoiding multiple layers. Figure 12 provides hardness values of the cross-section of both an Allomet TCHP coating used for a pin on disc test as well as a conventional WC-Co LMD coating for comparison. The average hardness of the TCHP coating is about 1700 HV1 with peak values measuring up to 2230 HV1. The average hardness of the WC-Co coating is about 1450 HV1 with peak values measuring up to 1750 HV1.

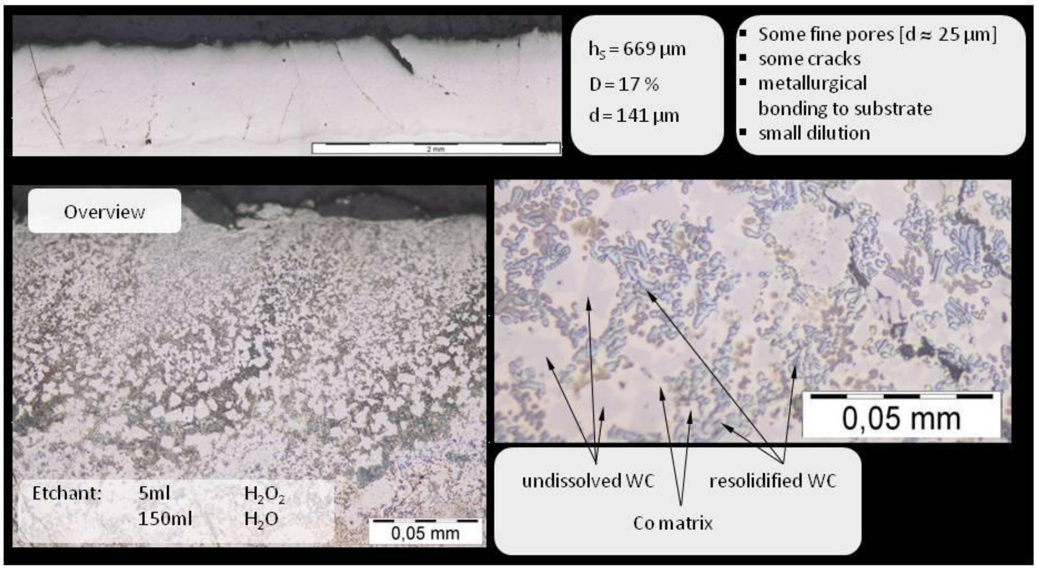


Figure 11: Allomet TCHP LMD coating cross-section: Top – overview showing cracks, Bottom – microstructure showing undissolved and resolidified WC particles.

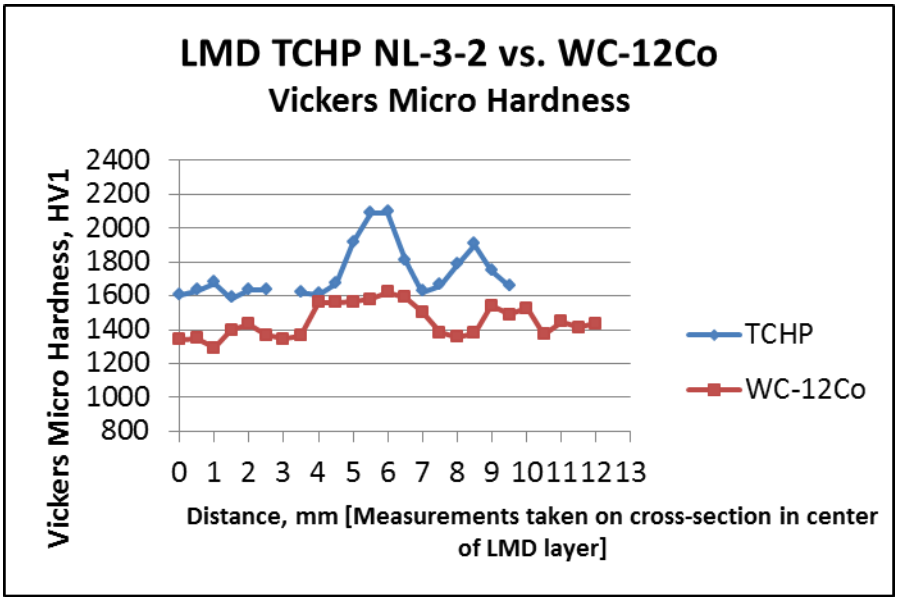


Figure 12: Microhardness of Allomet TCHP and of WC-12Co LMD coatings: Measurements were taken left to right across the cross-section of a sample used in a pin-on-disc test.

Also, a standard pin-on-disc test was performed on both Allomet TCHP and conventional WC-Co LMD coatings. The initial test shows excellent wear resistance against abrasion comparable to conventional cladded WC-Co. In fact, no measurable abrasive wear was observed for either material after 2000 meters. Thus, more rigorous evaluation is required to examine the full potential of laser deposited TCHP material as wear resistant coatings. Figure 13 provides hardness values of the Allomet TCHP coating surface used for the pin-on-disc test. The average hardness is about 1950 VH1 with peak values measuring up to 2570 HV1. Finally, the friction coefficient of both materials was similar, averaging 0.5µ.

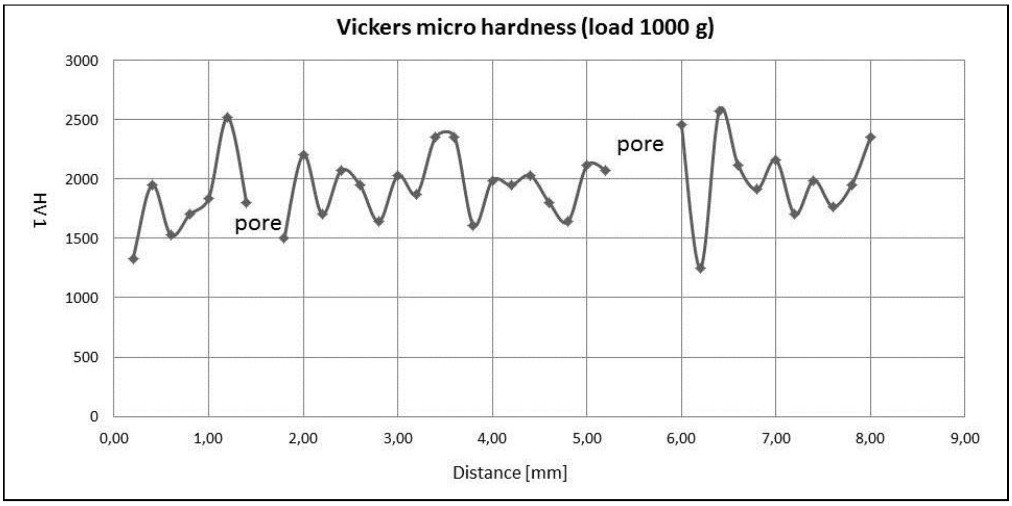


Figure 13: Microhardness of Allomet TCHP LMD coating: Measurements were taken across the surface of the sample used in the pin-on-disc test. Missing points labeled as “pore” may be cracks at the surface.

Although extremely high hardness values can be achieved using a TCHP-only LMD coating, the incidence for cracking was found to be high, and this may be undesirable for certain applications. Therefore, current development includes blending TCHP with metal matrix alloys to provide additional strength and ductility to a TCHP-based LMD coating. Preliminary trials have produced multi-phase microstructures, the potential performance benefits of which are being determined.

Looking Forward

New Grades of TCHP Materials

Allomet is currently developing new grades of TCHP materials that address specific market needs. The most recent addition to the TCHP portfolio is a diamond “core” particle encapsulated with a shell of tungsten carbide, and subsequently, a cobalt layer. This new TCHP composition, along with several others that are under development, allows Allomet to produce specific mechanical and thermal properties in order to address specific applications. In the case of wire drawing, one diamond TCHP grade is expected to have a toughness well above that of standard PCD, and a hardness and thermal conductivity that far exceed any conventional tungsten carbide dies. These targeted material properties should increase the robustness of standard PCD dies and also lead to significantly lower wire – die interfacial temperatures during operation than those of conventional tungsten carbide dies. As the portfolio of TCHP materials continues to grow, Allomet will strive to address technical market challenges and expand the envelope of new material development.

Conclusion

Allomet Corporation’s Tough Coated Hard Powders (TCHP), or EternAloy® is a viable material system for producing coatings with a highly uniform microstructure, high hardness, and with porosity values at less than 1%. Similarities between TCHP surface coatings and TCHP sintered microstructures indicate a potential for providing improved wear resistance as observed in wire drawing applications. Allomet TCHP can be applied using a variety of techniques, including HVOF, LMD, and Plasma Spray. Current development work includes blending TCHP with metal matrix alloys to provide additional strength to TCHP-based LMD coatings.

References

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2. J.M. Keane and R. N. Wright, *Wire Journal International*, “Commercial Evaluation of TCHP Dies”, Vol. 45, No. 8, pp. 72-77, (2012)