# Sinter-Brazing of Carbides to P/M Steel

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## Abstract:

This study has investigated sinterbonding of carbide layers to traditional iron-based P/M parts during the sintering process. Materials selection trials led to further study with the $Cr_3C_2$-BNi5 system in vacuum, $H_2$ and $N_2/H_2$ atmospheres. The coating is created by first applying the carbide with a small amount of braze mixed in, then applying the braze powder on top. During the P/M steel sintering cycle, the braze melts and infiltrates the porosity of the carbide layer, and bonds it to the steel substrate. Spray application and electrophoretic deposition were investigated as potential application methods for this process.

## Background:

Wear resistant nickel and cobalt based materials have been applied to steels for many years [1,2]. These materials have a high volume fraction of carbides bindered by nickel or cobalt based alloy. Most of these coatings require temperatures above 1200°C for application by supersolidus liquid phase sintering. Conventional sintering of pressed P/M steels is typically performed in the temperature range of 1140 - 1170°C. This allows for interparticle bonding with without shrinkage, nearly maintaining the dimensional precision of the pressed component. To achieve bonding of a hard layer during a typical P/M sintering cycle, lower temperature binder materials must be used. This work investigates the use of Ni based braze alloys to infiltrate and bond a carbide layer to P/M steel.

The use of Ni based braze alloys to produce composite coatings has been achieved by other researchers [3,4]. These coatings utilize WC-Co as the hard phase, with a Ni-B braze alloy for infiltration. Lu et al [5] used tape casting to apply a WC-Co layer, and Ni brazing alloy BNi-2 layer to steel, and sinter braze the coating at 1120°C in vaccum. The bonding strength and wear properties were superior to thermal sprayed coatings of similar chemistry. This work investigates several application methods for green coatings,

including spray deposition, tape casting, and electrophoretic deposition (EPD). Spray deposition of powders does not lend well to highly contoured surfaces, since the process is line-of-sight, uneven coating thickness results. This is also true of thermal spray processes. EPD is a process in which a DC charge is applied across a suspension of charged particles, attracting them to an electrode of opposite charge. Ions in solution can adsorb to the particles and increase the charge on the particle, dramatically increasing the deposition rate. If the particles that are deposited are insulating, such as carbides and ceramics, the coating thickness becomes self-regulating at a given voltage. This allows for production of uniform coatings on complex geometries. Furman, et. al. [6-8] used EPD to apply $Cr_3C_2$, Ni, and B with an $Al(NO_3)_3$ ionic additive to the surface of wrought steel, and sinter brazed the deposition. The ionic additive speeds the process by increasing the charge on the particles. The B caused liquid phase sintering, which bonded the layer and eliminated porosity. Much work has been done in the area of EPD of ceramics, with the hopes of producing components and cermets [9]. Dissolved polymers such as polyvinyl butyral have been used to aid in the dispersion of particles in solution and to increase the handling strength of the deposition [10].

## Experimental Procedure:

Transverse rupture bars (3.2 cm x 1.3 cm x 0.8 cm) of P/M steel were pressed to achieve a density of approximately 6.9 g/cc. The alloy composition was Fe-0.85% Mo (prealloyed) + 2 wt. % Novamet 123 Ni + 0.6 wt. % C with an additional 0.6 wt. % Acrawax C. Initial coating trials were performed to determine material suitability. The bars were coated with a water based binder slurry of $Cr_3C_2$ and doctor bladed to a thickness of 0.25 mm. $Cr_3C_2$ was chosen because the thermal expansion coefficient matches well with Fe as compared to other carbides. The bars were then covered with four different braze tapecasts of various thicknesses to determine which alloy and weight ratio performed best. The four braze types were BNi-1a, BNi-4, BNi-5, and BNi-9. The individual braze alloy information is listed in Table I.

Table I – Braze Alloy information

| Alloy | Material Composition | Alternate Designations(s) | Solidus - Liquidus |
|---|---|---|---|
| BNi-1a | Ni + 14Cr + 4.5Si + 3B + 3Fe | AMS 4776 | 977-1077 °C<br>1790-1970 °F |
| BNi-4 | Ni + 3.5Si + 2B | AMS 4779<br>B50TF-26 | 982-1066 °C<br>1800-1950 °F |
| BNi-5 | Ni + 19Cr + 10Si | AMS 4782<br>B50TF-81 | 1079-1135 °C<br>1975-2075 °F |
| BNi-9 | Ni + 15Cr + 3.5B | AMS 4764 | 829- 927 °C<br>1615-1700 °F |

An approximate powder weight of each braze alloy was determined for each specific thickness of braze tapecast, using the solids loading and powder density. Similarly, the weight of $Cr_3C_2$ in the 0.25 mm layer was calculated to be approximately 0.38 g. The braze:carbide weight ratios are given in Table II.

Table II – Braze:carbide weight ratios

| Tape Cast Thickness, mm | BNi-1a/ $Cr_3C_2$ Weight Ratio | BNi-4/ $Cr_3C_2$ Weight Ratio | BNi-5/ $Cr_3C_2$ Weight Ratio | BNi-9/ $Cr_3C_2$ Weight Ratio |
|---|---|---|---|---|
| 0.20 | 0.75 | 0.82 | 0.80 | 0.79 |
| 0.25 | 0.94 | 1.02 | 1.00 | 0.98 |
| 0.30 | 1.13 | 1.22 | 1.20 | 1.18 |
| 0.38 | 1.41 | 1.53 | 1.50 | 1.47 |

Debinding was performed by heating in a retort furnace in $H_2$ at 5°C/min to 100°C, 1°C/min to 200°C for 1 h, 1°C/min to 300°C for 1 h, 1°C/min to 400°C for 1 h, 1°C/min to 450°C for 1 h, and furnace cooling. Sintering was performed at $10^{-3}$ Torr in a graphite construction furnace by heating at 5°C/min to 1160°C for 30 min, and cooling at 5°C/min. Sintering was also performed on selected samples in $H_2$ and 80%$N_2$ / 20%$H_2$ atmospheres in a CM alumina tube furnace by heating at 10°C/min to 1160°C for 30 min and cooling at 10°C/min. The sintered bars were cut, mounted, and polished for metallography.

Spray application of braze, carbide, and mixed braze and carbide layers was achieved with an automotive paint spray gun, with a high solids loading nozzle. A mixture of methanol and thinner was used along with a water-based binder. The methanol provided fast drying of the layer to prevent the coating from running down sidewalls. The powder solids loadings were 30-40 volume %, depending on the powder or powder mixture used. A rotating stage was used to achieve even coverage over the transverse rupture bar sidewalls and top surface.

Electrophoretic deposition was achieved in both IPA and ethanol with $Cr_3C_2$ and $Cr_3C_2$ / braze mixtures on the transverse rupture bars. Constant voltages of 50 - 150 V were applied for 3 – 30 minutes, depending on additive salts and coating thickness desired. Metal salt additives AlN, AlCl, and $MgCl_2$ were used to speed the deposition process.

## Results and Discussion:

In the initial screening experiments of the four candidate braze alloys, BNi-1a appeared to wet the $Cr_3C_2$ well but did not infiltrate and bond to the steel except in the case of the largest braze/carbide ratio. In the remaining BNi-1a samples, the carbide layer lifted up away from the bar, as shown in Figure 1. This indicates poor wetting behavior of the braze with the steel. BNi-4 appeared to not wet the $Cr_3C_2$, because most of the braze was left beaded up on the surface, as shown in Figure 2. BNi-5 infiltrated the $Cr_3C_2$ very well and infiltrated and bonded to the steel with all braze/carbide ratios. As the ratio increased, more porosity was eliminated in the steel and carbide layers, and a braze interlayer began to build up. This trend is observed in the micrographs given in Figures 3-5. This system is flexible in braze/carbide ratio because excess braze simply fills the

porosity of the steel. The BNi-9 bonded well for all braze/carbide ratios, however, the braze alloyed with the steel, resulting in over-grown pores. The pores become larger as the braze/carbide ratio increased. This trend is observed in the micrographs given in Figures 6-8. The boron in the braze alloy most likely caused a depression in the melting point of the steel, causing over-sintering to occur, and large rounded pores result. This would most likely result in poor mechanical properties. Based on these results, BNi-5 was chosen for spray deposition and electrophoretic deposition trials.

The microhardness of the BNi-5 infiltrated $Cr_3C_2$ coating measured 70 HRC (converted). The infiltrated interlayer of steel and braze measured 26 HRC, while the base porous steel measured 24 HRC, due to porosity.

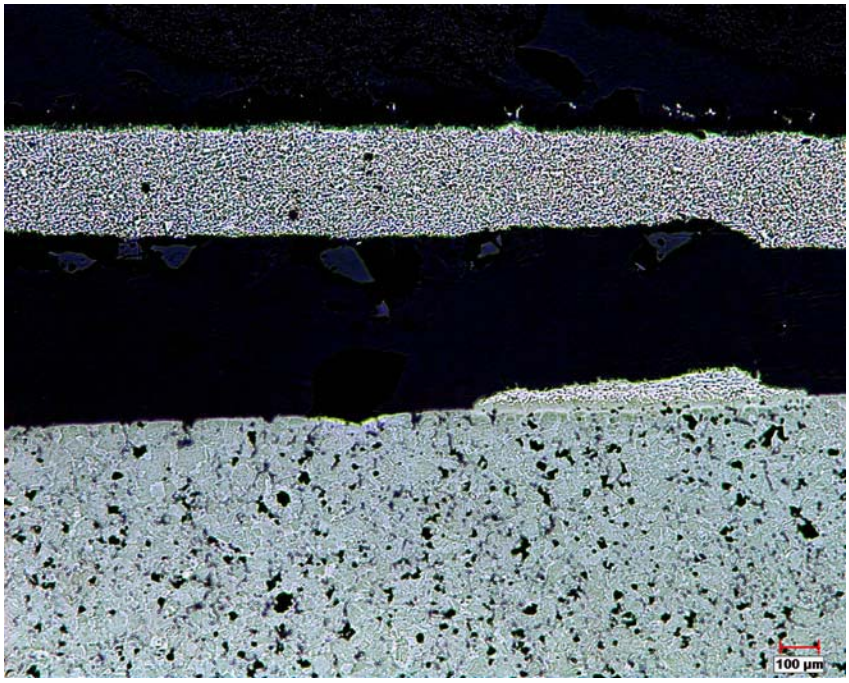


Figure 1. BNi-1a – $Cr_3C_2$ coating on P/M steel with a braze/carbide ratio of ~1.1. Coating (top) is fully infiltrated, but did not bond well to steel (bottom).

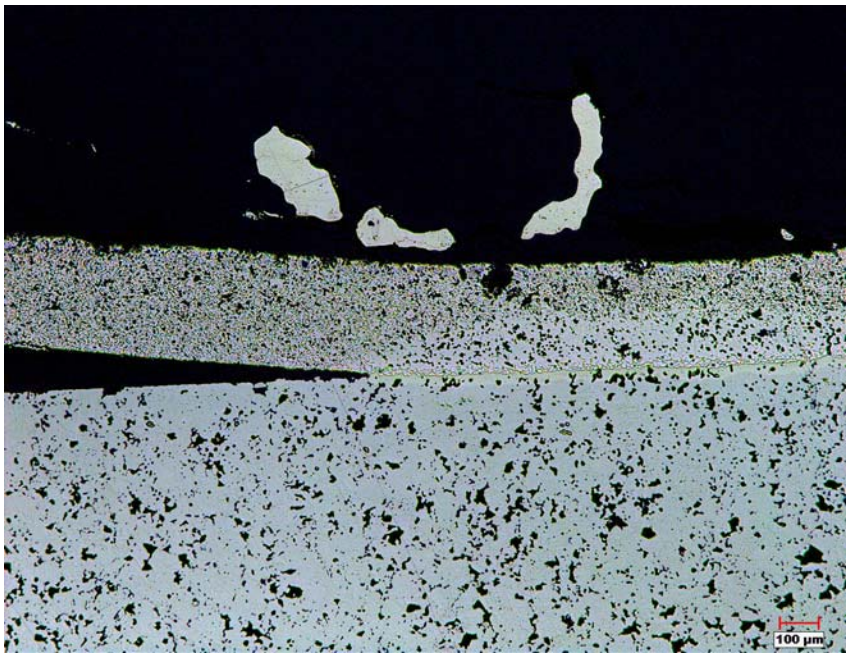

Figure 2. BNi-4- $Cr_3C_2$ coating on P/M steel with a braze/carbide ratio of ~0.8. Material on top is braze alloy that did not infiltrate the carbide layer (middle), which is still porous.

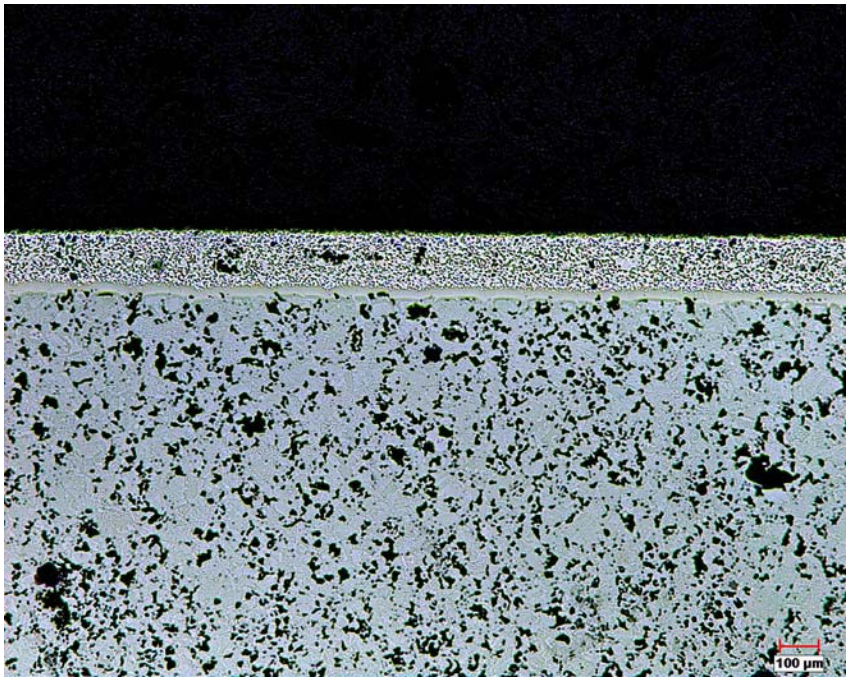

Figure 3. BNi-5- $Cr_3C_2$ coating on P/M steel (bottom) with braze/carbide ratio of ~0.8. Coating is bonded, but steel is not infiltrated.

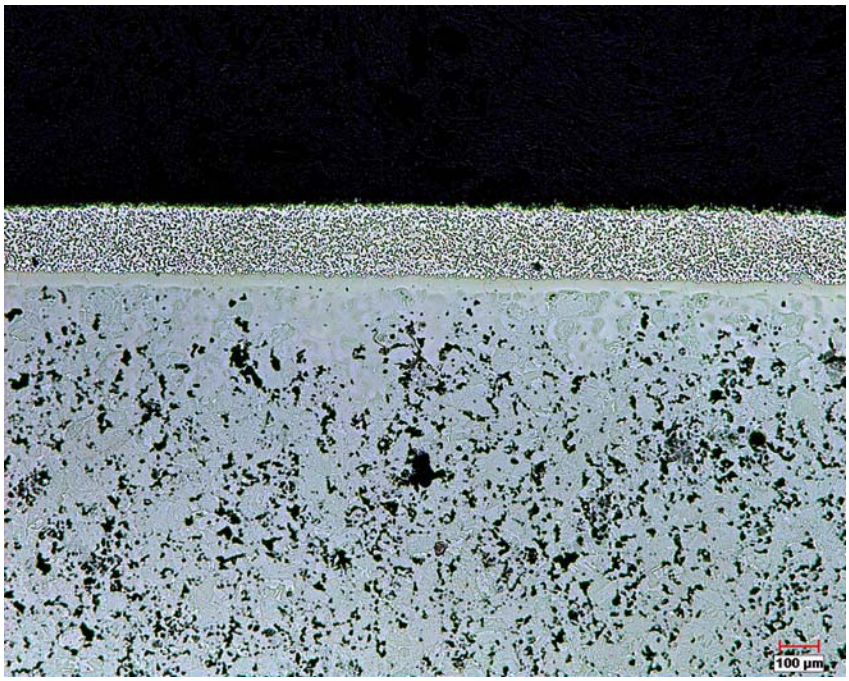

Figure 4. BNi-5- $Cr_3C_2$ coating on P/M steel (bottom) with braze/carbide ratio of ~1.2. The pores in the steel adjacent to the coating is partially infiltrated.

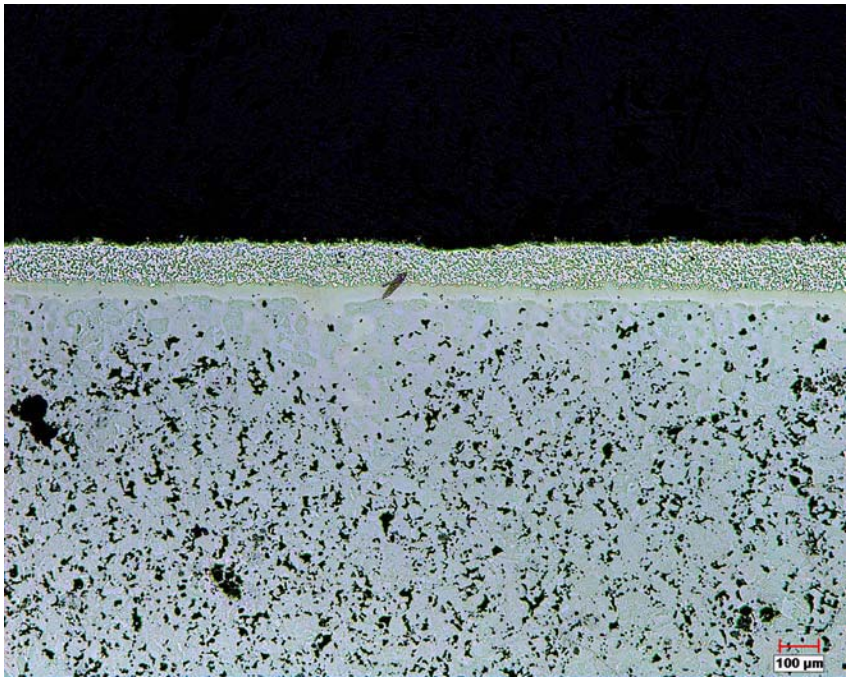

Figure 5. BNi-5- $Cr_3C_2$ coating on P/M steel (bottom) with braze/carbide ratio of ~1.5. The pores in the steel adjacent to the coating is partially infiltrated, and the braze layer between the steel and coating is thicker than observed in Figures 3 and 4.

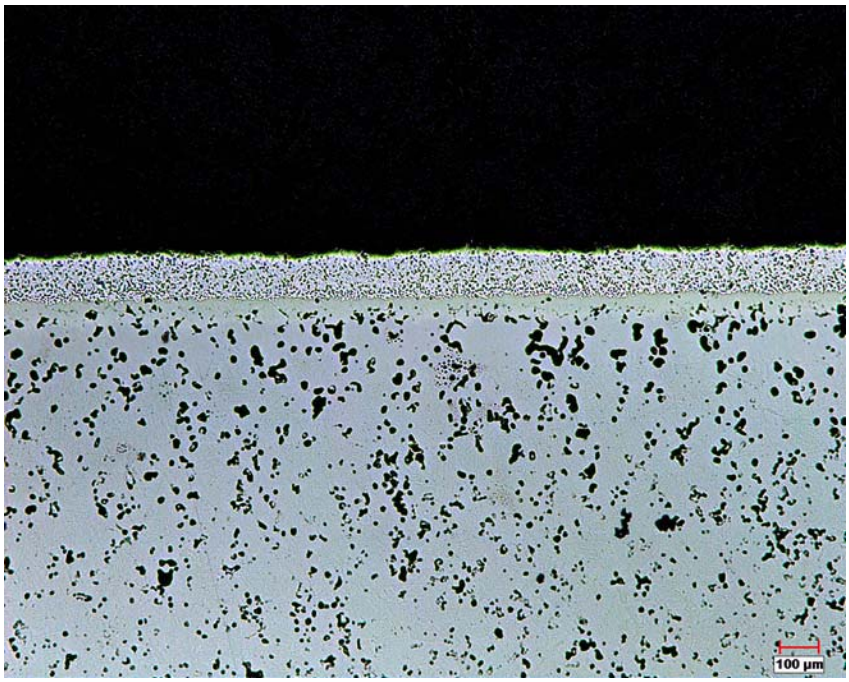

Figure 6. BNi-9 - $Cr_3C_2$ coating on P/M steel (bottom) with a braze/carbide ratio of ~0.8. Slight spherodization of pores in the P/M steel near the coating.

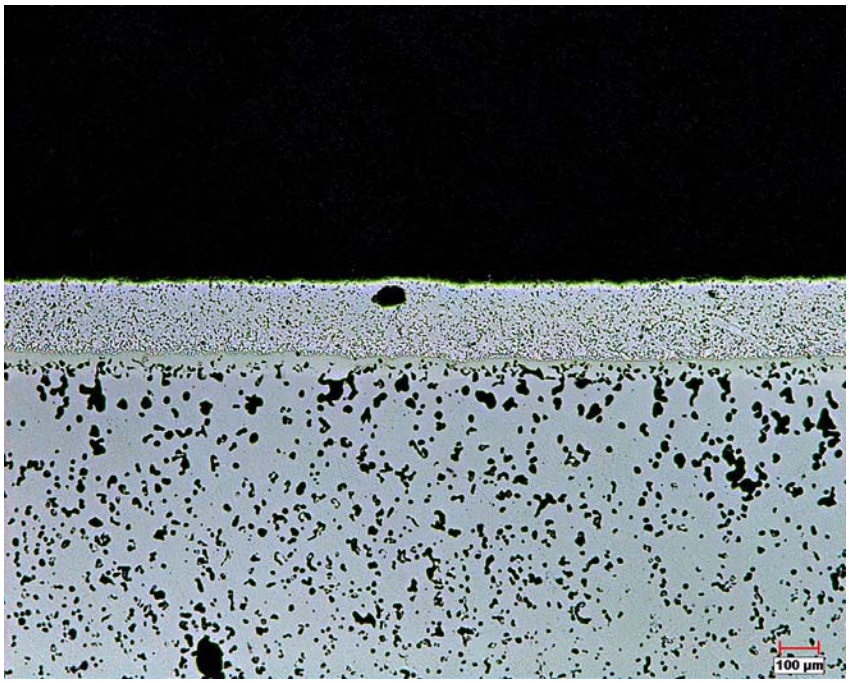

Figure 7. BNi-9 - $Cr_3C_2$ coating on P/M steel (bottom) with a braze/carbide ratio of ~1.0. Spherodization and growth of pores in the P/M steel near the coating.

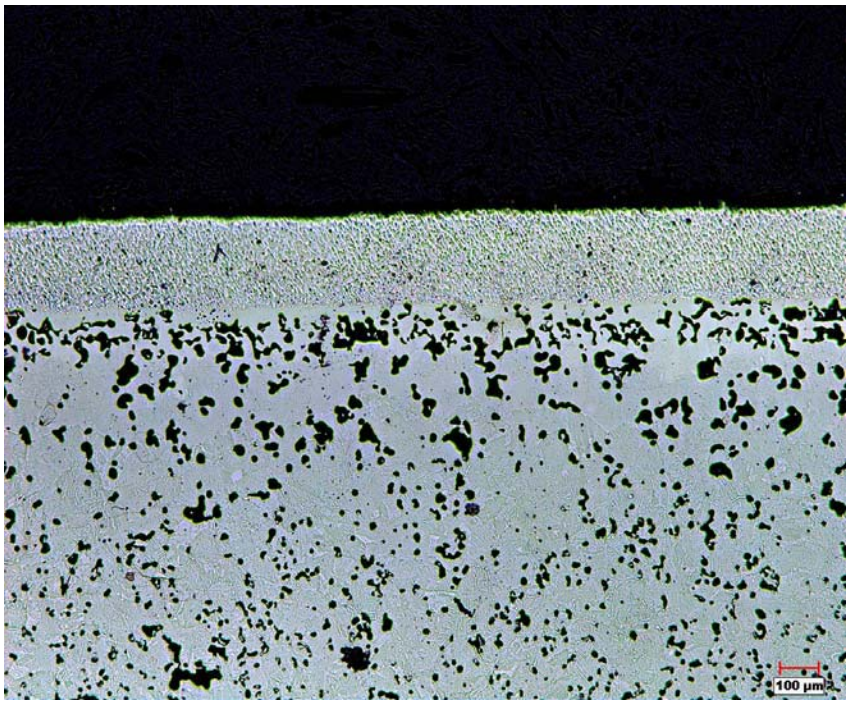

Figure 8. BNi-9 – $Cr_3C_2$ coating on P/M steel (bottom) with a braze/carbide ratio of ~1.5. Increased spherodization and growth of pores in the P/M steel near the coating.

Spray coating resulted in good sintered coatings on the TRS bars, however, controlling the coating thicknesses and smoothness was difficult. Pure carbide and 80% carbide / 20% braze mixtures were employed in the base layer. As seen in Figure 9, the coating is uniform, but significant rounding of corners results. Coatings were successfully sintered in $1x10^{-3}$ Torr vacuum, $H_2$, and 80% $N_2$ / 20% $H_2$ atmospheres. Best results were achieved when the weight ratio of base layer to braze layer was ~1:1. The occurrence of debonding defects was greater in the case of 80% $N_2$ / 20% $H_2$ atmosphere.

The wear characteristics of the spray coated material was compared to the wear characteristics of heat treated wrought 4140 steel with a hardness of 56 HRC, indicating far superior wear properties in the coating. The weight and volume losses in the coating were 0.12 g and 0.016 $cm^3$. The weight and volume losses in the heat treated 4140 were 1.13 g and 0.14 $cm^3$.

In initial trials, electrophoretic deposition (EPD) was achieved with pure carbide and 80% carbide / 20% braze mixtures. SEM images were taken of the 80/20 mixed powder that was deposited on a sample, to determine if both powders were deposited. The image showed both spherical braze particles and angular carbide particles, indicating that both particles were deposited, but the proportions may have been altered from the original mixture. Pycnometry of the deposited powder indicated a density closest to the density of the carbide, indicating that the bulk of the deposit was carbide. Particle size analysis of the deposit and comparison to the original powder particle sizes indicated that the smaller particles deposited, likely due to the easy suspension and motion of small particles. Figures 10 is a micrograph of a sintered EPD carbide coating with the braze layer applied by spray application. In some areas, the coating thickness was not uniform,

often bumpy. Coating uniformity was improved by the use of $MgCl_2$ as an ionic additive rather than $Al(NO_3)_3$.

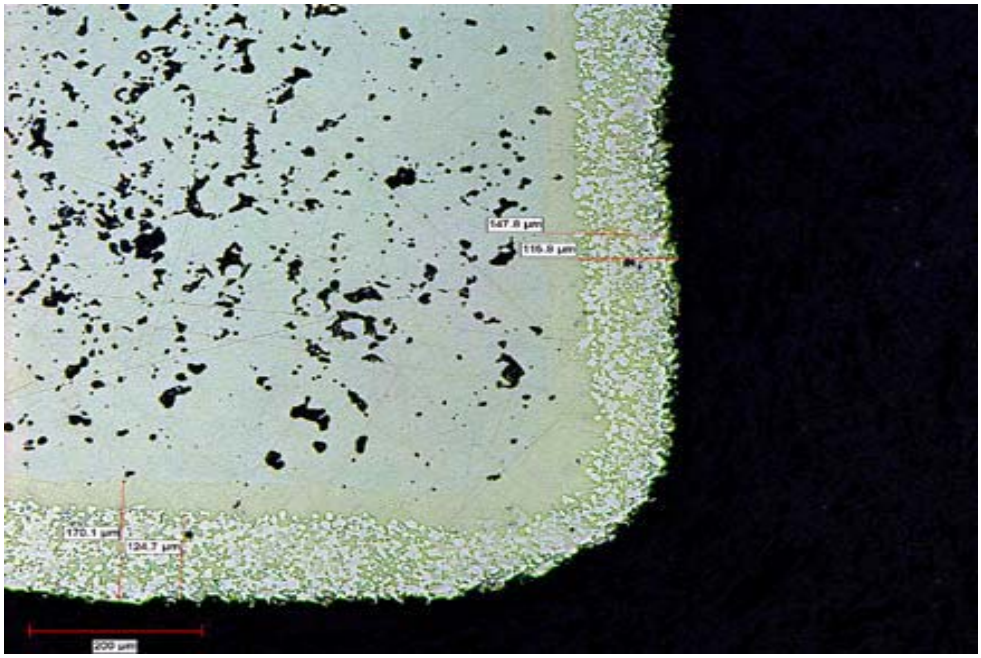

Figure 9. Sprayed two-layer coating, vacuum sintered at 1160°C, showing corner rounding.

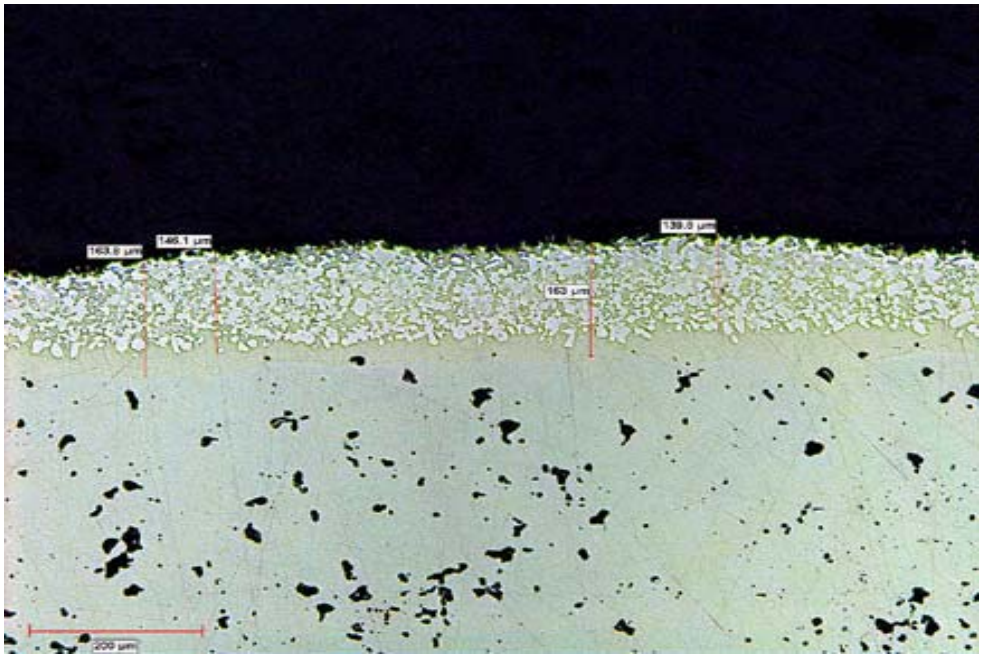

Figure 10. Sintered EPD carbide coating with sprayed braze coating, vacuum sintered at 1160°C.

## Conclusions:

Carbides may be sinter-brazed onto pressed P/M steel in vacuum, $H_2$ or $N_2/H_2$ atmospheres. Best results are achieved in vacuum or $H_2$ sintering. Good wettability of the braze alloy to the carbide, and to the P/M steel are critical to obtaining a robust system. Coatings may be applied by spray application or electrophoretic deposition.

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