Brush Plating a Metal Matrix Composite: Cobalt - Chromium Carbide

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Metal matrix composite coatings can improve the surface properties of a material beyond the capability of the substrate, the composite material or the metal alone. The high temperature performance of a cobalt metal - chromium carbide particle composite coating, which can be applied by several methods, provides protection against oxidation and wear. This work investigates the application of a Co-Cr_3C_2 metal matrix composite by brush plating. The Cr_3C_2 particles were highly dispersed and suspended in the cobalt sulfate electrolyte through effective agitation. The particles were electrophoretically deposited along with cathodic deposition of cobalt. The distribution of the Cr_3C_2 particles throughout the composite coating was observed to be uniform by x-ray fluorescence and by optical and scanning electron microscopy. The electrodeposited composite coating showed improved characteristics including superior hardness and wear resistance. The Co-Cr_3C_2 coating demonstrated oxidation protection and an increase in hardness upon exposure to temperatures up to 815°C. The abrasive wear resistance measured with a Taber abraser also improved after a high temperature exposure. The adhesion of the coating to the substrates was strong in part due to a nickel interlayer used to enhance the bond between the substrate and the coating. The residual stress of the Co-Cr_3C_2 composite coating on a steel substrate was found to be much smaller than that of a cobalt metal coating. This work demonstrates that brush plating can be used to apply a high performance coating to a select area on a substrate.

Keywords: *Selective plating, metal matrix composite plating, cobalt-chromium carbide deposition*

Introduction

A metallic-ceramic or metal matrix composite (MMC) can offer unique and superior characteristics including hardness, wear resistance and oxidation protection at high temperatures with respect to a metal or an alloy. A MMC coating can improve the surface properties of a material beyond the capability of the substrate, the composite material or the metal alone. There are several potential methods to apply the MMC on metal substrates such as e-beam, sputtering, thermal spray and chemical vapor deposition (CVD), etc. Those methods require high temperatures, high vacuum or high melting-point for the substrate. By contrast, electroplating is a convenient and effective method for applying a MMC coating onto a basis metal.

Electroplated MMC has been used for high temperature performance materials[1] and for replacement of plated hard chromium.[2] Among metal-matrix composite coatings, plated Co-Cr_3C_2 has been attractive, because, besides the merits mentioned above, its thermal expansion coefficient (TEC) is very close to that of steel (a common basis material). A small

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difference in TEC between the coating and substrate reduces the mechanical stress built up at the boundary when exposed to high temperatures.

Kedward[1] pioneered the work of tank plating of MMC Co-Cr_3C_2 for coating components of turbine engines. However, successful deposition of MMC Co-Cr_3C_2 coating using brush plating has not been reported. Brush plating is complementary to tank plating because it has advantages such as more flexible and convenient operation and faster deposition. In order to expand the application of MMC Co-Cr_3C_2 coatings, it is important to achieve the coating by selective brush plating.

There are some difficulties in achieving the MMC coatings by brush plating. For example, the ceramic particles, chromium carbide (Cr_3C_2) are difficult to suspend in the circulating electrolyte, which is generally a smaller volume than the electrolyte used for tank plating. Furthermore, the particles can be trapped inside the brush or the anode cover and stagnate on the route of electrolyte circulation, hindering their return to the solution reservoir for recirculation. Recent research has made significant progress in these areas for brush plating the MMC on various substrates. The present paper elaborates on how robust MMC Co-Cr_3C_2 coatings were achieved by selective brush plating through enhancement of electrolyte agitation and circulation, and adjustment of anode design and other operation parameters.

Experimental

A cobalt plating solution containing 80 g/L Co^{+2}, added as cobalt sulfate heptahydrate, and sulfuric acid at pH 1.5 was made using technical grade chemicals followed by filtering through activated carbon. Ceramic powders, chromium carbide (Cr_3C_2) of particle size 1 - 6 µm were added to the solution as received. The concentration of Cr_3C_2 in the solution was controlled between 300 and 500 g/L. Deionized water was used for solution makeup and rinsing.

Cr_3C_2 particles were insoluble in the cobalt solution and normally settled to the bottom of the reservoir because of their high mass density (6.70 g/cm^3). A suspension of the particles was achieved by ultrasonic agitation and gas stirring. A peristaltic pump was used to circulate the electrolyte solution to the gap between the anode and the cathode. Stagnation of the ceramic particles along the route was prevented by a funnel or sloped pan to induce particle movement back to the solution reservoir for recirculation. The MMC plating was conducted at room temperature and up to 40°C. The current density was tested in the range of 0.3 – 1.20 A/cm^2. A SIFCO rectifier, Model CP-II 60-25, supplied adjustable plating current and was capable of switching between anodic and cathodic polarities rapidly upon sequence requirement. Figure 1 shows a setup for brush plating a MMC onto a panel. Other geometries were plated with a similar setup.

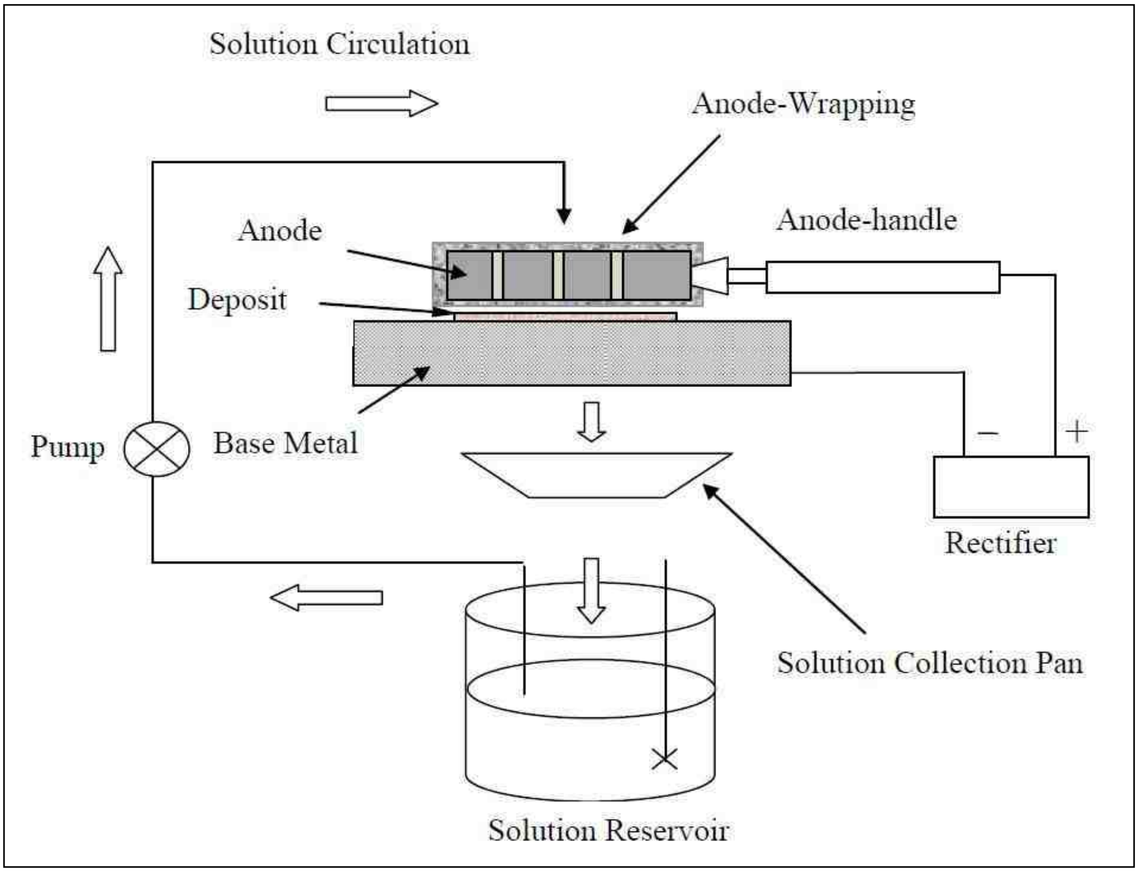

Figure 1 - Diagram of the process of brush-plating MMC onto a metal surface.

Separate anodes were used for the surface preparation and the MMC deposition though the construction of both anodes was similar. A noble metal-coated titanium mesh supported by a polypropylene or graphite block is shown in Fig. 2. Holes drilled through the block allow solution (or suspension) to flow through the anode structure onto the work piece. Anode cover materials with different porosities were employed in the tests. The anode-to-cathode distance was determined by the thickness of the anode cover material, which was approximately 5 mm.

The characteristics of the MMC deposit on various substrates measured were adhesion, surface finish, hardness, Taber wear index and residual stress. The adhesion tests included tape-pull, repeated bend, thermal cycling and machining. The surface finish (roughness) was measured using a Mahr profilometer (Pocket Surf PS1), the hardness with a Vickers hardness tester, and Taber wear following ASTM D 4060-95. Residual stress was measured using x-ray diffraction by Proto Manufacturing. The cross-sectional analysis was conducted using optical and scanning electron microscopy. X-ray fluorescence was used to determine the concentration and distribution of the carbide in the deposit.

Results and discussion

Mechanism

The electrochemical deposition reactions in the cobalt sulfate-based electrolyte are:

$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ on the anode (1)

$Co^{+2} + 2e^- \rightarrow Co$ on the cathode (2)

Chromium carbide powder did not dissolve in the solution to form ions (cations or anions). The carbide particle was electrophoretically co-deposited along with cobalt on the cathode. These particles were small, in the range of 1 – 6 µm. Such small particles normally tend to agglomerate to each other. Therefore, it is important to use adequate agitation or stirring to break or prevent agglomeration and keep the particles highly suspended and dispersed in the solution for electrophoresis.

Carbide particle distribution

The distribution of carbide particles throughout the metal matrix was examined using optical micrographs and SEM images of cross-sections of plated parts. A uniform distribution of ceramic particles in the metal matrix is shown in Figs. 3 - 5. The rounded or squared asperities are chromium carbide particles encased in metallic cobalt. The micrographed deposits are as polished, without a microetch.

The surface of the as-plated composite had a matte grey appearance. X-ray fluorescence analysis indicated the distribution of Cr_3C_2 across the deposit was uniform within ±3 wt%. The Cr_3C_2 content in the deposit could be as high as 50 wt%. The carbide content was controlled between 10 and 50 wt% through adjusting deposition parameters. Since different end use applications may require different contents of Cr_3C_2, the control of Cr_3C_2 content is important.

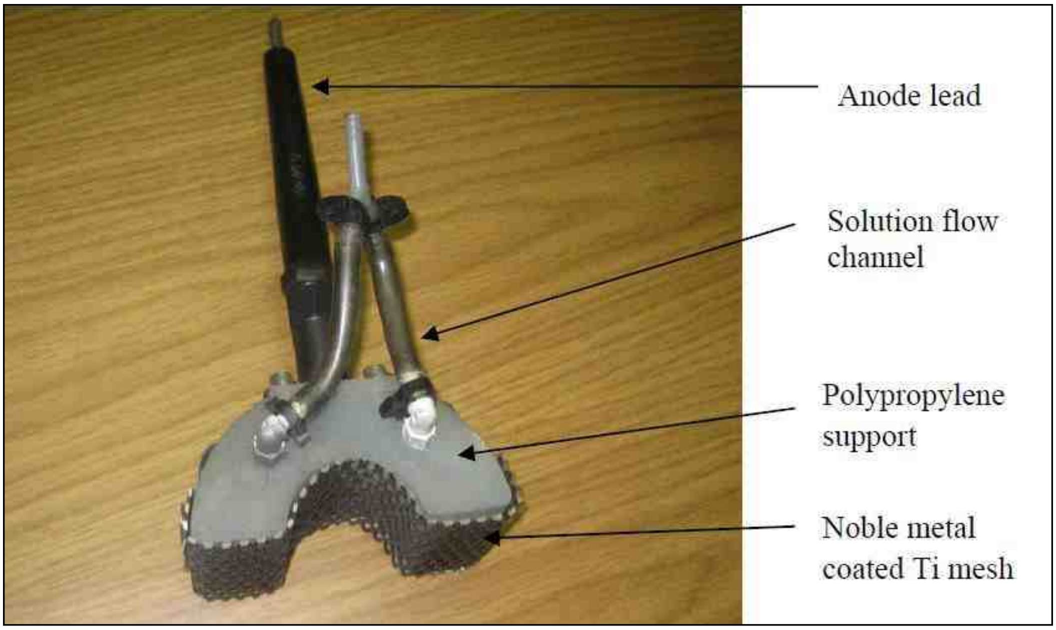

Figure 2 - Anode for brush plating MMC onto a ring or pipe.

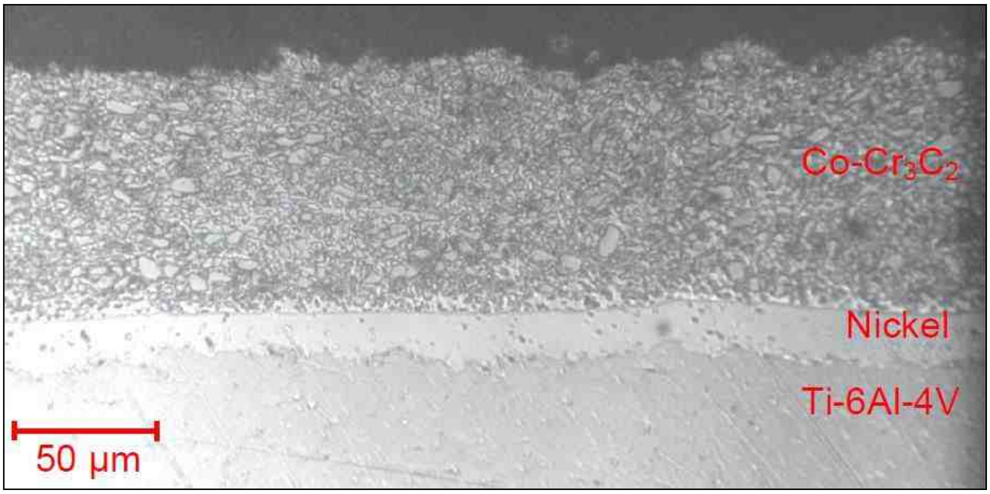

Figure 3 - Optical cross-section of the Co-Cr$_3$C$_2$ coating on titanium alloy containing 33 wt% Cr$_3$C$_2$.

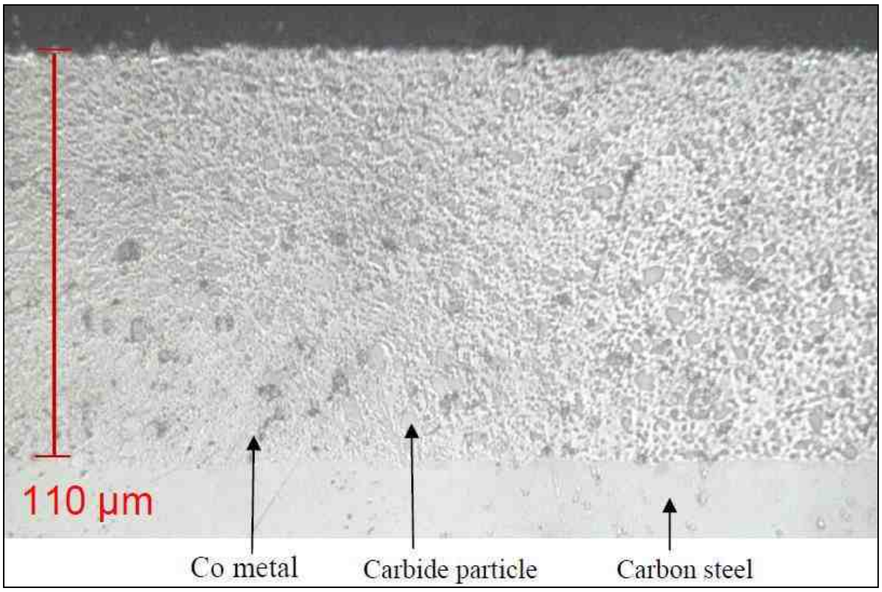

Figure 4 - Optical cross-section of the Co-Cr$_3$C$_2$ coating on carbon steel containing 19 wt% Cr$_3$C$_2$.

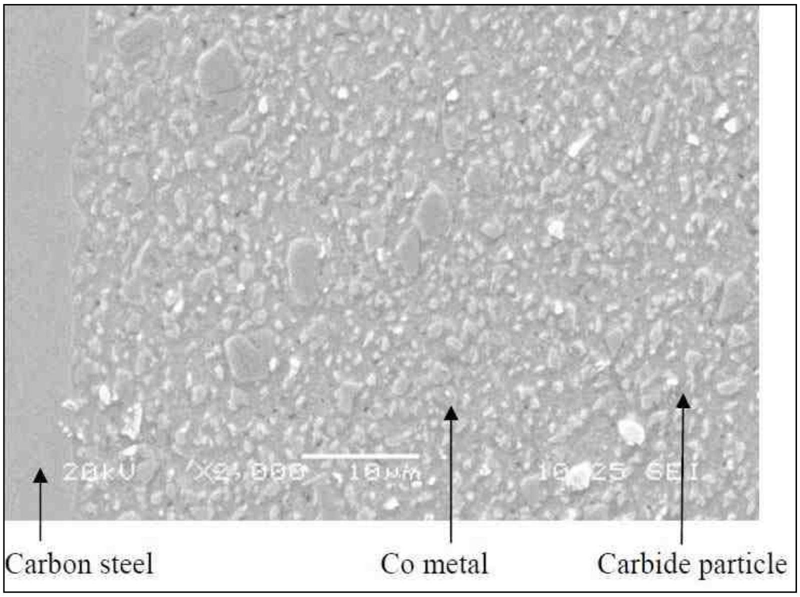

Figure 5 - Secondary scanning electron microscope image of a Co-Cr$_3$C$_2$ deposit on steel in cross-section at 2000× magnification.

Adhesion

The cobalt chromium-carbide composite deposit has shown good adhesion to a wide range of substrates. The adhesion was enhanced and assured by an intermediate nickel bonding layer plated prior to the MMC plating. The MMC deposit on all substrates used (such as carbon steel, stainless steel, Inconel, Ti-6V4Al) passed tape, bending and machining tests with good adhesion. The MMC did not flake off the basis metals like steel and Ti-6Al-4V alloy after numerous thermal cycles between room temperature and 800°C. This could also partially be attributed to a relatively small difference between the thermal expansion coefficients of the coating and the basis materials.[4]

Hardness

The cobalt chromium carbide coating has shown microhardness values from 360 to 500 VHN (Vickers hardness number) as deposited whereas the hardness of plated cobalt is around 360 VHN. Pure chromium carbide, known to be very hard with 1200 VHN, contributed to the increase of the hardness. The carbide particles in the cobalt metal matrix serve as the aggregates contributing to the higher hardness, whereas the metal matrix functions like a carrier for the hard aggregates. The higher the chromium carbide content in the deposit, the harder the deposit should be. However, this trend did not always appear in the brush plated deposits. The size of the carbide particle may have had a role in contributing to the hardness.

The thermal stability of the Co-Cr_3C_2 composite was tested by heat treatments at a series of temperatures up to 815°C. The results are shown in Table 1. Hardness measurements indicated the Co-Cr_3C_2 composite was thermally stable. Typically after heating a pure metal to an elevated temperature, the hardness of the metal decreases. The hardness of the composite did not decrease after heating to elevated temperatures. In fact, a somewhat higher hardness was measured after heat treatment.

Table 1

Hardness (VHN) of Co-Cr_3C_2 deposit after a one-hour heat treatment

Wt% Cr_3C_2	As deposited	Heat treatment temperature		
		400°C	750°C	815°C
12 - 15	442	505	498	485
25 - 30	418	485	476	482

Normally a metal coating is oxidized upon exposure to high temperature. The MMC Co-Cr_3C_2 coating exhibited a strong oxidation resistance at high temperatures. A MMC Co-Cr_3C_2 plated steel panel after exposure to 800°C for 30 hr did not show any sign of being oxidized in the plated area, Fig. 6. A Ti-6Al-4V panel showed yellow dust indicating some extent of oxidation occurred after 1 hr at 800°C. A steel panel was severely oxidized after exposure to 800°C for 1 hr.

Taber wear index

The Taber wear tests were performed following ASTM Test Method D 4060-95. The wear index (µg/cycle) is calculated as follows:

$$\textit{Wear Index} = \frac{(A-B)1000}{C} \tag{3}$$

where A is the weight of test specimen before abrasion (mg), B is the weight of the test specimen after abrasion (mg), and C is the number of cycles. A 1000-gram load was applied to each CS-17 abrasive wheel.

Taber wear index data for the MMC Co-Cr_3C_2 coating, uncoated Ti-6Al-4V and steel panels are presented in Fig. 7. The MMC Co-Cr_3C_2 coated material has a significantly lower wear rate than uncoated Ti-6Al-4V and carbon steel. The decrease in wear index as the number of cycles increases is believed to be due to a decrease in the roughness of the coating. The roughness of the as-plated deposit is decreased by the abrasive action of the CS-17 wheels. A smoother surface has a lower wear rate.

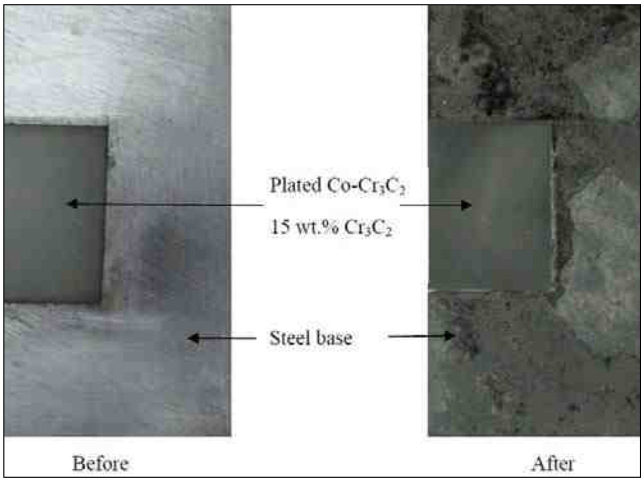

Figure 6 - Surface appearance of a Co-Cr_3C_2 plated steel panel before and after exposure to 800°C for 30 hr.

The Taber wear index for a cobalt metal-coated panel is compared to a MMC Co-Cr_3C_2 coating in Fig. 8. The wear index of the composite coating was significantly lower than that of plated cobalt metal.

Exposure to an elevated temperature of 400°C leads to a significant decrease in the wear index of the composite coating, Fig. 9. This data further confirms the good high temperature performance of the brush plated Co-Cr_3C_2 composite coating. The Ti-6Al-4V wear index is not changed by exposure to this elevated temperature.

Residual stress

The residual stress of a coating is an important factor in the reliability of the plated part. It may influence the performances of coatings such as the resistance to spalling, delamination and surface cracking. The residual stress of MMC Co-Cr_3C_2 on titanium 6Al-4V alloy measured by x-ray diffraction is presented in Table 2. The residual stress of the MMC coating on steel substrate measured by the bent strip method is also presented in the table. The residual stresses were tensile. The residual stress of Co-Cr_3C_2 coating was less than that of plated cobalt metal. The high residual stress appears to be due to the cobalt metal and not the chromium carbide or its combination with the cobalt metal matrix.

The coating showed larger residual stress on the steel substrate than on the Ti-6Al-4V substrate, suggesting that the residual stress of the coating may be influenced by the substrate. This could be due to different interfacial tension building up between the coating and different substrates.

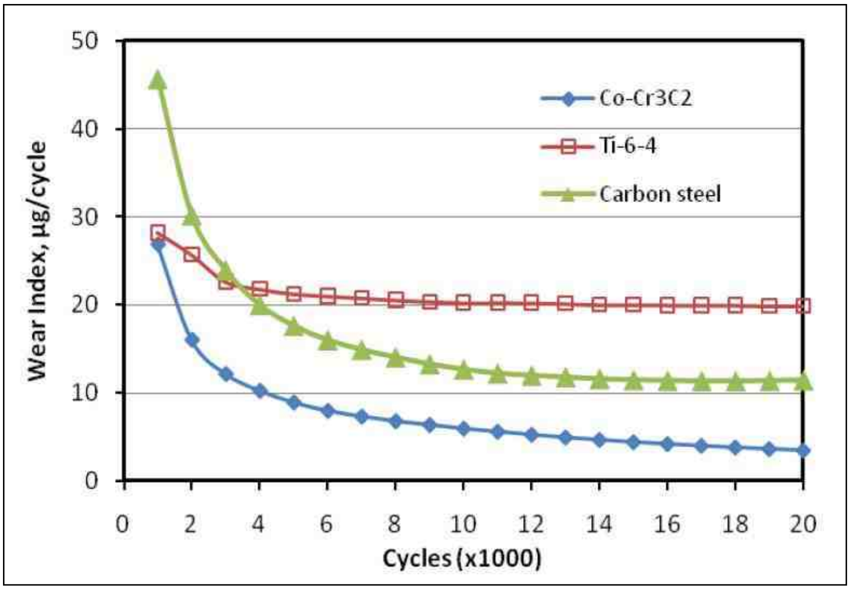

Figure 7 - Taber wear index measured for MMC Co-Cr_3C_2,Ti-6Al-4V and carbon steel.

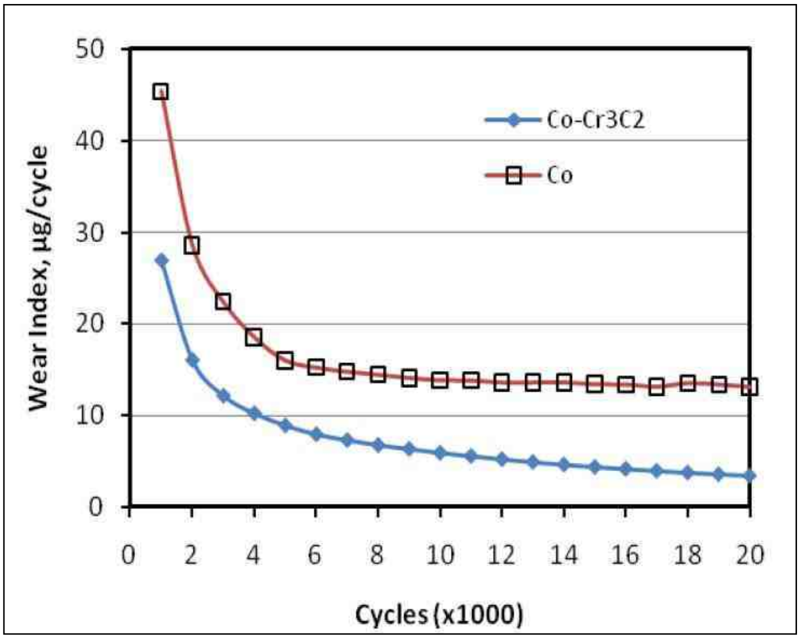

Figure 8 - Taber wear index measured for MMC Co-Cr_3C_2 coating and metallic cobalt coating.

Table 2

Residual stress of Co-Cr_3C_2 and Co coatings on Ti-6Al-4V alloy determined by XRD and on steel calculated from deflection measured for coated strips

Coating	Stress, kpsi (on Ti-6-4)	Stress, kpsi (on steel)
Co-Cr_3C_2	31 ± 3	36 ± 5
Co	33 ± 3	70 ± 5

It was observed that the residual stress of the MMC coating was also dependent on the plating process. Low cathode current density gave lower residual stress. However, change of anode wrapping material (*i.e.*, brush) had little influence on the residual stress of the MMC coating.

Key characteristics

Table 3 summarizes the key characteristics of the cobalt-chromium carbide brush-plated composite. The performance of the Ti-6Al-4V alloy and steel were improved by a brush-plated MMC coating. The MMC improvements are more significant than those of a cobalt metal-plated coating especially after exposure to high temperature. The improved surface characteristics should lead to increased resistance to fretting, adhesive wear and abrasive wear.

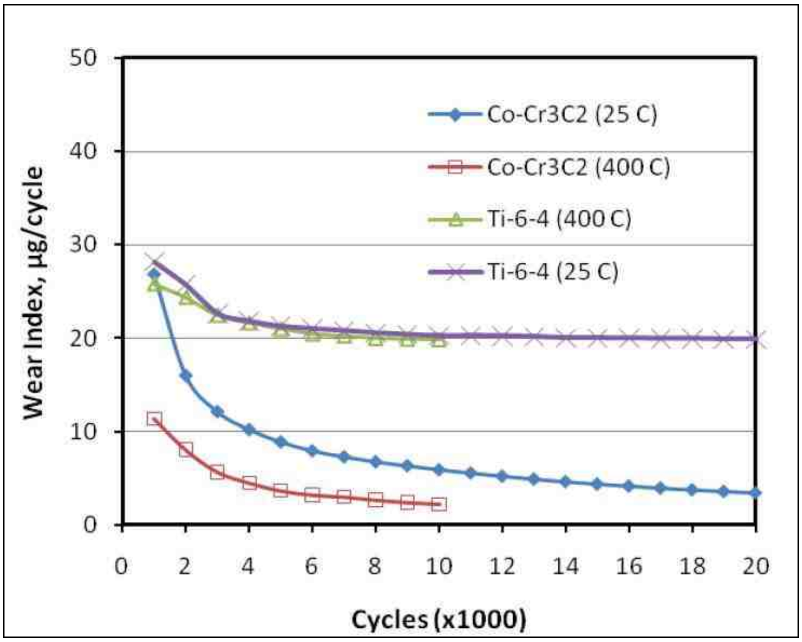

Figure 9 - Taber wear index for MMC Co-Cr_3C_2 and Ti-6Al-4V before and after exposure to 400°C.

Conclusions

A metal matrix composite, Co-Cr_3C_2 was brush-plated on various substrates. The adhesion of the MMC deposits to the substrates was strong and passed all adhesion tests. The distribution of the carbide particles throughout the cobalt metal matrix was uniform and the carbide content in the deposit was controlled between 10 and 50 wt%, depending on the application's requirement. The MMC coating showed good hardness and strong resistance to wear and oxidation at high temperatures.

Table 3

Key characteristics of the brush plated metal-matrix composite Co-Cr_3C_2 coating compared to brush plated cobalt and unplated substrates

Property	Unit	Brush-plated Co-Cr_3C_2	Brush-plated cobalt	Ti-6Al-4V	Carbon steel
Cr_3C_2	wt%	10 – 50	0	0	0
Uniformity of Cr_3C_2	wt%	± 3	-	-	-
Microhardness	VHN	360 – 500	360	330	150
Hardness change after 400°C exposure	%	> + 10 %	> - 10%	> - 5%	> - 15 %
Taber wear index	µg/cycle	8.0	17	21	16
Taber wear index after 400°C exposure	µg/cycle	4.0	15	21	17
Surface finish as deposited, R_a	µm	0.5 - 1.5	0.5 - 1.5	-	-

References

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About the authors

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Dr. Haiming Xiao *received his Ph.D. in electrochemistry from the Norwegian Institute of Technology (Trondheim) in 1993. Following his doctoral study, he performed post-doctoral studies at the University of Tennessee (Knoxville). He then worked at Oak Ridge National Lab, Rosemount Analytical Inc. and Wright Patterson Air Force Research Lab in the areas of materials science and electrochemical systems. In 2008, he joined SIFCO Applied Surface Concepts as an R&D engineer.*

Dr. Sid Clouser *is a Research and Development Manager at SIFCO Applied Surface Concepts. He has a Ph.D. in electrochemistry from Case Western Reserve University. During 29 years in industrial electrochemical research he has coauthored papers, made presentations at technical conferences and is a co-inventor on numerous patents. The group of professionals he works with at SIFCO support the design, manufacture and marketing of selective deposition processes on a worldwide basis.*

People in the News

Brett Larick named as Columbia Chemical President

Columbia Chemical, a leader in the zinc and zinc-alloy plating industry, has announced that **Brett Larick** has been named President. In his new role, he will oversee Corporate Development including developing and implementing competitive and corporate strategies, growth and profitability, innovation and value creation, and leadership development within management groups. Larick succeeds Bill Rosenberg, who will continue serving as Chairman of the Board and Marketing Director.

Rosenberg ensures a smooth transition of leadership responsibilities, “Brett is highly capable and well equipped to take this company to the next level.” He continues, “He brings the significant experience and expert knowledge needed to direct those initiatives.”

Larick began his 17-plus years of industry experience as a technical sales and support representative. He joined Columbia Chemical in 1999 as Sales Manager, a leading force in the company’s domestic sales development resulting in continual significant growth of domestic direct business. In 2004, he was appointed Vice President of Sales, with expanded focus on global collaborative opportunities. Larick holds a B.S. degree in Chemistry from Cleveland State University and recently completed the distinguished Executive MBA Program at Case Western Reserve University.

“I am looking forward to the challenges ahead in leading Columbia Chemical as we continue our growth in the metal finishing industry.” Larick said. *P&SF*