Deposition of Hard Chrome Coating onto Heat Susceptible Substrates by Low Power Microwave Plasma Spray

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Deposition of Hard Chrome Coating onto Heat Susceptible Substrates by Low Power Microwave Plasma Spray

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Abstract. Microwave plasma spray requires relatively low power, which is lower than 1 kW in comparison to other plasma spraying method. Until now, we are able to deposit Cu and Hydroxyapatite coating onto heat susceptible substrate, CFRP which are difficult for conventional plasma spray due to the excessive heat input. In this paper, a hard chromium coating was deposited onto SUS304 and CFRP by a low power microwave plasma spray technique. By controlling the working gas flow rate and spraying distance, a hard chrome coating with thickness of approximately 30 μm was successfully deposited onto CFRP substrate with hardness of 1110 $Hv_{0.05}$. Furthermore, the coating produced here is higher than that produced by hard chrome plating.

1. Introduction

Hard chrome plating is a crucial process associated with manufacturing and maintenance operations on aircraft, vehicles and ships, both in civilian and military sectors. Hard chrome electroplating is commercially used to produce wear-resistant coatings but the plating bath contains hexavalent chromium, which has adverse effects on health and environment. For this reason, the use of hexavalent chromium has been limited [1]. The types of coating methods that are most widely viewed as being capable of replacing hard chrome plating are the thermal spray technologies [2, 3]. Plasma spray method is the most versatile in the thermal spray technologies where even high melting point materials such as ceramics coating can be deposited. However, the conventional plasma spray method generates high heat input (8000 ~ 15000 K in plasma region) to both substrate and spray materials especially to the heat susceptible materials [4]. For this reason, the research of depositing hard chrome coating by low power plasma spray method has been brought upon.

Low power plasma spray method [5] is defined as a thermal spray method which used the thermal plasma generated with low input power (less than 10 kW) in the heat source. The effects of lowering the input power of the thermal spraying equipment by the plasma production at low electric power as well as the effects of controlling the heat input to the spray material (control of the significant change of material's microstructure) by low input power plasma are expected and the research is advancing in recent years. However, the input power of Cu coating deposited by conventional DC plasma spray method under atmospheric pressure condition which was reported is

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approximately 5kW [6, 7], while deposition of coating by using RF plasma spray under atmospheric pressure condition is reported to be difficult due to the difficulty in stabilizing the plasma. On the other hand, with the input power of less than 1 kW, thermal plasma generation under atmospheric pressure is possible for microwave plasma spray method [8]. For this reason, it is thought that the coating deposition in which the heat input to the thermal spray material can be suppressed is achievable by applying microwave plasma as a low power plasma spray process. Moreover, this microwave plasma does not require electrode for electric discharge, which made it possible to generate plasma from chemically reactive type of gases if being compared to DC plasma in which the electrodes are needed for electric discharge. In comparison to DC plasma, microwave plasma has a lot of advantages such as plasma can be produced with relatively low input power, high plasma density, wide discharge frequency and electrodeless gas discharge [9]. Therefore, in recent years, microwave plasma was applied in a wide range of fields, such as decomposition processing of harmful gas, heat treatment of waste, sterilization of medical material, and deposition of thin film [10]. In our laboratory, the low power atmospheric pressure microwave plasma spraying device which used microwave plasma for the heat source was successfully being applied [11].

Under atmospheric pressure, the plasma production of approximately 1 kW of low input power is made possible by the atmospheric pressure microwave plasma spraying device. Moreover, in order to investigate whether the heat input reduction to the spray substrates is possible, the metal (Cu) coating deposition onto low melting point material called carbon fiber reinforced plastics (CFRP) and fiber reinforced plastic (FRP) which are susceptible to heat, is already clarified [12]. In case of coating deposition of hydroxyapatite (HA) as a biomedical material, emergence of decomposition phase harmful to human body caused by the heat input from the plasma will occur for the conventional plasma spray process [13, 14]. However, the HA coating with suppressed decomposition phase is also successfully able to be deposited [12].

Here, we deposit a hard chrome coating onto heat susceptible substrate, CFRP by using low power microwave plasma spray. For comparison, a hard chromium coating was also deposited onto SUS304. Morphologies and structural characteristics were measured by using X-ray diffraction (XRD) and scanning electron microscope (SEM).

2. Experimental procedures

2.1 Process and materials

2.1.1 Process

The experimental system of the atmospheric pressure microwave plasma spraying is shown in Figure 1. Microwaves with the frequency 2.45GHz are transmitted through a rectangular waveguide and oscillated into a cylindrical resonant cavity by a hollow antenna on the axis. Working gas of Ar is mixed with spray particles in an aerosol chamber and supplied axially through the antenna. The system generates high-intensity electric field on the tip of the antenna, induces electrical breakdown of working gas, and plasma plume is generated at the downstream. The spray particles are heated and accelerated by the plasma plume, and the coating is deposited by the impact of spray particles onto substrate surface at downstream. In this experiment, the experimentation of coating deposition and the observation of as-sprayed coating in which Cr powder was used as the spray particle, the observation of splat's shape, coating composition and the measurement of the hardness of coatings were performed. Experimental conditions are shown in Table 1. Working gas flow rate and spray distance were changed in order to investigate the possibility of coating deposition. Coating was first deposited onto high melting point substrate which is SUS304, and after considering the most suitable parameter for the coating deposition onto heat susceptible material, the coating was fabricated onto CFRP substrate. The coating was deposited onto SUS304 and CFRP in order to compare the coating formation onto metal substrate and composite substrate and to study the mechanism involved in both materials.

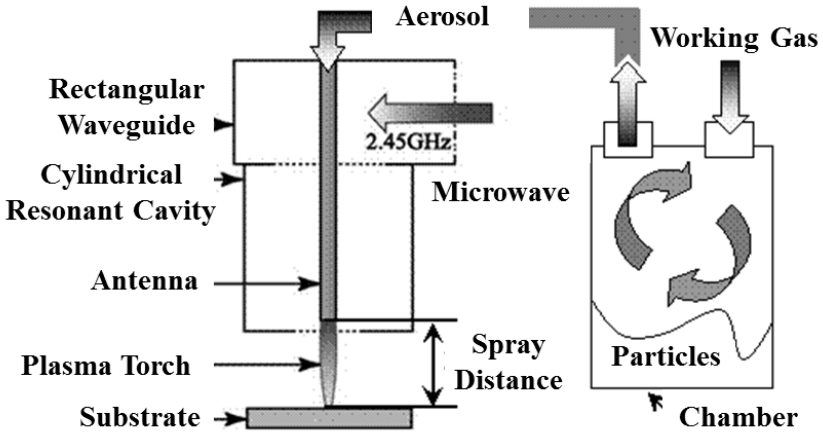


Figure 1. Schematic diagram of low power atmospheric pressure microwave plasma spray system.

Table 1. Experimental conditions for the deposition of Cr coating

Input power (kW)	0.5
Working gas flow rate (l/min)	15, 19
Antenna outlet diameter (mm)	1.5
Spray distance (mm)	30, 35, 40
Traverse speed (mm/s)	5
Deposition time (s)	300

2.1.2 Materials

In this experiment, high hardness metal material, Cr which possesses the melting point of 2176 K is used as feedstock powder to deposit coatings. The Cr powder (ATP100-10μm, KOJUNDOKAGAKU Research Centre) has the average size of 10 μm with the purity of above 98%. SEM image of Cr powder is shown in Figure 2. After the experimentation of the coatings deposited onto SUS304 substrates, coating was deposited onto heat susceptible substrate, CFRP at the most suitable condition. The CFRP substrates used is with unidirectional carbon fiber composition and the melting point temperature is about 523K. As the pre-treatment for the substrates before spraying, the surface of the substrates was cleaned by ethanol. Size for both kinds of substrates was set at the dimension of 20 mm x 20 mm x 3 mm.

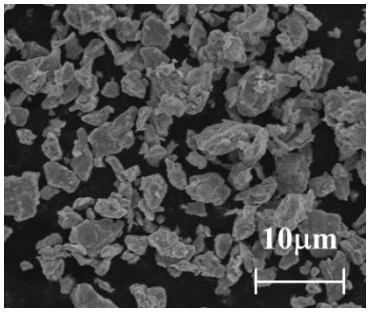
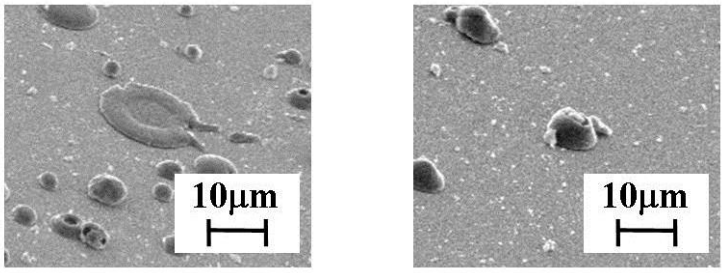


Figure 2. SEM image of Cr particles.

2.2 Evaluation methods

Observation of coating surface and cross section was conducted using scanning electron microscope (SEM: JSM-6390TY, JEOL Co. Ltd.). The observation of the impinged form of the splat onto the substrates for each experimental condition was conducted, and the appearance ratio of the particle impinged onto the substrates was investigated. Figure 3 shows the SEM image of the fully-melted and half-melted splat form of the particles impinged onto the substrates. The consideration of the fully melted splat form is defined as the particles which fully impinged onto the substrates and possess splat diameter of more than 10 μm while for the half-melted particles, impinged particles must at least have the size of more than 5 μm. The particles which passed the specifications which defined beforehand will be calculated and the flattening ratio is defined as the ratio of the fully-melted and half-melted particles per the sum of the collected particles. Substrate temperature was measured at the position of 1.0 mm from the surface of the substrate by K-type thermocouple. The hardness of as-sprayed coatings was measured by micro-hardness measurement device (HMV-1). The micro-hardness measurements were carried out on a polished cross section of the coatings with an applied load of 490.3mN and test time was 10 s. The indentation was performed at 7 different places and the average value was calculated. The distance between indentations was large enough to avoid interaction between the work-hardened regions and any micro-cracks caused by the indentations. The occurrence of oxides in the deposited coatings was verified by X-ray diffraction analysis (XRD: RINT-2500, Rigaku), with CuK radiation.



(a) (b)

Figure 3. SEM image of (a) fully-melted and (b) half-melted splats collected at spray distance of 30 mm and 40 mm respectively with constant working gas flow rate of 19 l/min.

3. Results and Discussion

3.1 Cr coating deposition

Figure 4(a) shows the SEM image the top view surface morphologies of sprayed particles impingement onto SUS304 substrate. The hard chrome coating was first deposited onto SUS304 substrates in order to study the possibility of Cr coating deposition by microwave plasma spray onto a much higher melting point material than CFRP. From the result, Cr particles were observed to be melted and impinged onto the SUS304 substrate, and the splat was uniformly fabricated onto the SUS304 substrate. The cross-sectional morphology showed that the chrome coating of the coating deposited at optimum condition with working gas flow rate of 19 l/min and spay distance of 30 mm is shown in Figure 4(b). This spraying condition is considered optimum due to the highest thickness and the uniformity of the coating formed. From the cross-sectional observation, Cr coating with the thickness of approximately 50 μm is able to be deposited onto SUS304 substrate. From the results, it is clarified that the deposition of high melting point chrome coating onto SUS304 is possible at 0.5 kW of input power. The Cr particles were observed to be sufficiently melted and adhered directly to the surface of SUS304 substrate without any void in between the coating and substrate's surface.

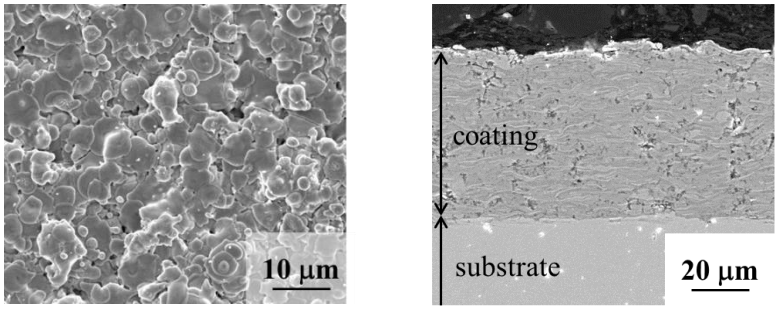


Figure 4. SEM images of the deposited coating onto SUS304 substrates at (a) top view, and (b) cross sectional view.

Figure 5 shows the correlation of gas flow rate with substrate temperature and spray distance. The substrates temperature decreased with the increase of spray distance and irrespective of the working gas flow rate. At a constant spray distance, the substrates temperature was lower with gas flow rate of 19 l/min compared to that of 15 l/min. By using working gas flow rate of 19 l/min, the substrate temperature is observed to be below the melting point temperature of CFRP materials irrespective of the spray distance. This is due to the reduction of the plasma length resulting from higher working gas flow rate. An increase in working gas flow rate induced the reduction of the energy given per unit working gas volume at constant microwave energy, resulting in decrease in plasma length because of the thermal pinching effect [15].

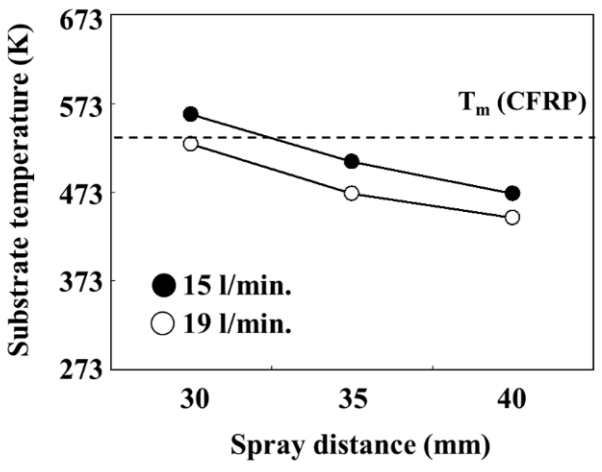
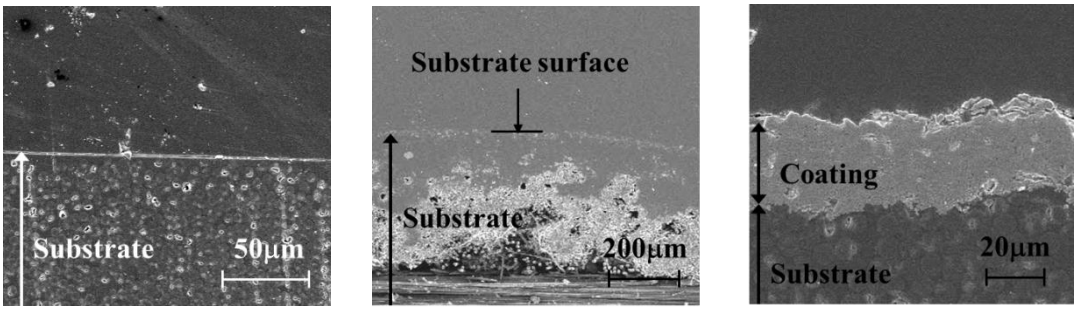


Figure 5. Correlation of gas flow rate with substrate temperature and spray distance.

Deposition of coating was performed onto CFRP substrates at spray distance 30 mm which possesses the highest coating thickness and lowest substrates temperature. Figure 6(a) shows the SEM image of the cross-sectional morphology of CFRP substrate, while the results of cross-sectional morphology of Cr coating deposited under each spray conditions are shown in Figure 6(b) and Figure 6(c). From these results, on the conditions of working gas flow rate 15 l/min, the emergence of the holes inside the substrate due the sublimation of the resin of the matrix of CFRP was observed. It is already clarified from the results of the study on substrates temperature in Figure 5 that the temperature is higher than the melting temperature of CFRP. Due to high heat input to the substrate material, it is thought that the coating deposition is difficult for this condition. On the other hand, on

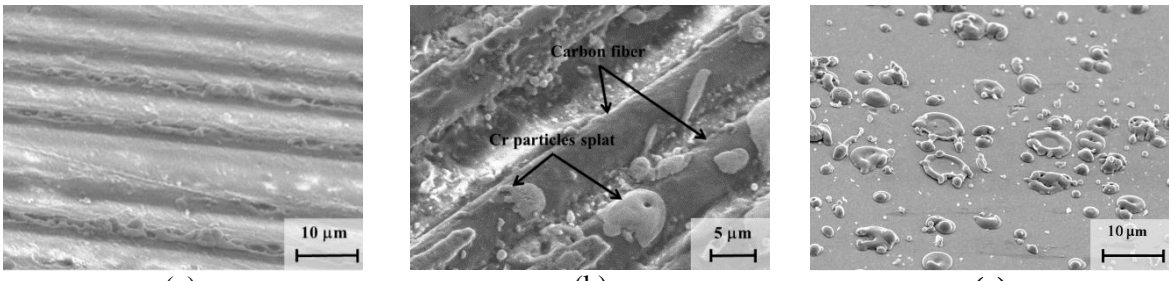
the condition of working gas flow rate 19 l/min, emergence of the hole by sublimation of resin inside the substrate is not occurred. It is considered that this is due to the reason that the substrates temperature under the conditions of working gas flow rate 19 l/min is 525 K, which is near to the heat-resistant temperature of CFRP. As a result of this phenomenon, the heat input to the substrates has been able to be controlled. Moreover, on the condition of working gas flow rate 19l/min, deposition of Cr coating is possible on CFRP substrates, and the thickness of the coating deposited is about 30 μm. However, since the film thickness of the obtained coating is decreased compared with the case where SUS304 is used as the substrate, it is thought that by roughening the surface thick coating was possible to be deposited. As compared with the surface of the substrate before spraying, on the surface of substrate after coating, particles have structure which penetrated into the substrate. It is thought that the resin which is a matrix of the substrate sublimates from the heat effect by the particles impinged onto the CFRP surface, and became uneven and bumpy structure. Therefore, from the concavo-convex field of the surface of substrates made by the impinged particles, it is thought that mechanical bonding becomes a major factor of the bond of the substrates and the coating in order the coating to be deposited.

Figure 7 shows the SEM morphologies of splat collected on CFRP and SUS304 substrates respectively at optimum condition which is at gas flow rate 19 l/min and 30 mm spray distance. Cr coating deposition rate is slower for the coating onto CFRP. This is due to the deposition mechanisms of the coating is different for the particular substrates type. From the observation, it is clear that the surface of SUS304 substrate is not changed during the spray and the fully flattened splat as well as the half molten particles is adhered to substrate surface. While on CFRP, the polymer part of the surface is slightly melted and the spray particles is observed to be more gathered at the area that is appeared to be the carbon fiber.



(a) (b) (c)

Figure 6. Cross-sectional SEM images of (a) CFRP substrate, (b) substrate condition after sprayed at 15 l/min, (c) coating deposited at 19 l/min



(a) (b) (c)

Figure 7. Oblique view of SEM morphologies of CFRP substrate (a) before spray, (b) after spray and (c) after spray onto SUS304 substrate

3.2 Evaluation of coatings

Since sufficient coating thickness was not obtained for the measurement of coating hardness under the conditions of working gas flow rate 15 l/min, only coating deposited under the conditions of working gas flow rate 19 l/min were used for the measurement of coating hardness. Figure 8 shows the results of coating microhardness. In all spraying distances, the hardness of the coatings is higher than 900 $Hv_{0.05}$ (average hardness of hard chrome plating). The coating deposited by microwave plasma spray reached the hardness not only comparable as Cr plating but also improved at certain spray conditions. Furthermore, coating hardness decreased with the increase in spraying distance, and it can be found that coating hardness showed the highest average value of 1110 $Hv_{0.05}$ under the conditions where the spraying distance is 30 mm. From this, it can be inferred that since the dense coating was formed of the particles in which sufficient flattening occurred with the increase in flattening ratio, coating hardness increased. Figure 9 shows the result of flattening ratio of Cr particles splat shape with the change of spray distance at working gas flow rate of 19 l/min. From the result, it is clarified that the flattening ratio is increased with the decrease in spray distance as a reason of the densification of the fabricated coatings which results in the increase hardness of the coating.

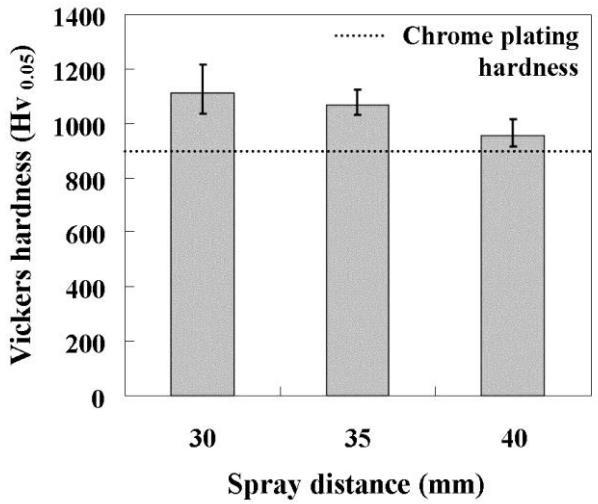


Figure 8. Vickers microhardness of Cr coatings with the change of spray distance.

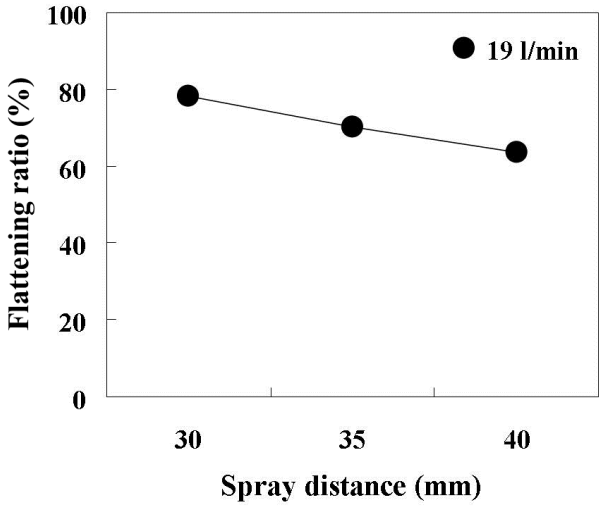


Figure 9. Flattening ratio of Cr particles splat shape with the change of spray distance.

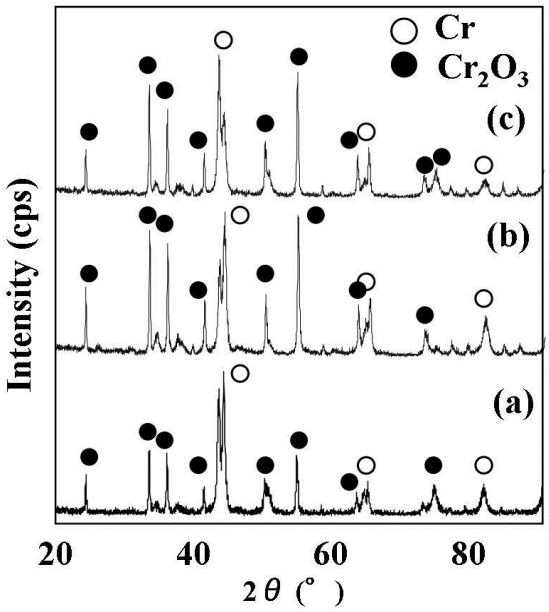


Figure 10. XRD patterns of Cr coatings at spray distance (a) 30 mm, (b) 35 mm and (c) 40 mm.

Composition analysis by XRD of the deposited coatings was conducted at spray distance of 30 to 40 mm at 19 l/min of working gas flow rate in which coating hardness measurement was performed. The results of XRD analysis of the as-sprayed coatings are shown in Figure 10. From the results, the peak of chromium (III) oxide which is an oxide of Cr was confirmed inside the coating irrespective of the change of spray distance. From this, it can be considered that the emergence of chromium (III) oxide during spray resulting in the high hardness of the coating due to the hardness of the chromium oxide. Moreover, it turned out that the peak intensity of chromium (III) oxide becomes higher with the increase of spraying distance. This is due to the increase of in-flight travelling time of the particles exposed into the atmosphere with the increment of spray distance, resulting in the increase of Cr particles oxidation.

4. Conclusion

We have demonstrated the deposition of chrome coating by low power atmospheric pressure microwave plasma spray onto SUS304 and heat susceptible substrates. The summary of the results and the characteristics evaluation are listed below.

1. The deposition of Cr coating onto SUS304 is possible by using low power atmospheric pressure microwave plasma spray at input power of 0.5 kW.
2. The hardness of the coating obtained at the optimum condition, at working gas flow rate 19 l/min are above 900 Hv0.05 which is higher than the hardness of hard Cr plating.
3. Cr coatings deposited by low power atmospheric pressure microwave plasma spray contain the oxide of chrome which contributes to the increase hardness of the coatings. The composition of chromium (III) oxide inside the coatings increased with spray distance and working gas flow rate.
4. Cr coatings with the thickness of 30 μm were successfully deposited onto heat susceptible substrates, CFRP by using microwave plasma spray device. The average microhardness of the deposited coating was 1110 Hv which is higher than hard chrome plating.

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