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Multilayered WC–Co/Cu coatings by warm spray deposition

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ABSTRACT

WC–Co/copper multilayer coatings consisting of 8 layers were fabricated by warm spray deposition in order to investigate the effect of ductile layer inclusion onto their fracture behavior. Bending strength, work of fracture, and surface hardness of freestanding coatings were examined by three point bending tests after removal of the substrates. The multilayered samples showed non-linear stress–strain curves due to crackings in the WC–Co layers and plastic elongation of the copper layers. The multilayered samples with lower volume fraction of copper showed even lower bending strength than the monolithic samples of WC–Co and copper and no beneficial feature in mechanical performance was found. On the other hand, the samples containing higher volume fraction of copper exhibited more than twice higher work of fracture and moderately better bending strength than the monolithic WC–Co coatings, while the surface hardness was almost identical among all samples instead of the monolithic copper. The ductility of copper layers and the plastic constraint by the intact WC–Co layers attributed to enhance their mechanical properties. It has been concluded that cermet/metal laminate coatings can be one alternative approach to further improvement of the mechanical properties of thermal sprayed cermet coatings.

1. Introduction

Thermally sprayed WC–Co coatings have been applied to various industrial components in order to protect them from aggressive environmental damages such as abrasive wear, erosion, and foreign object damages [1–3]. High velocity oxy-fuel (HVOF) spraying is one of the most popular deposition techniques of cermet coatings in recent days. While coatings deposited by HVOF show similar or even higher hardness of 1000–1300 Hv than sintered bulk WC–Co materials, their fracture toughness is much inferior to the bulk materials. The origins of the poor fracture properties are formations of brittle phases such as W_2C and η phase ($M_{12}C$ and M_6C) due to decarburization of WC and dissolution of W and C into Co binder during spraying.

In order to improve the fracture toughness and overall mechanical performance of WC–Co coatings, mainly two approaches have been taken. One is to deposit WC–Co coatings at lower process temperature and to suppress those detrimental reactions during flying of particles. Jacobs et al. [4,5] deposited WC–Co and WC–Co–Cr coatings by high velocity air-fuel (HVAF) spraying. The coatings did not show the formation of brittle phases. While the hardness of HVAF WC–Co was decreased, the WC–Co–Cr coating showed improved hardness and wear resistance. Kim et al. [6] successfully applied cold spray (CS) deposition to fabricate WC–Co coatings without the detrimental phases mentioned above. While the coatings exhibited extremely high hardness of 1820–2050 Hv, the overall performances of these coatings such as toughness and wear properties are still unknown. Watanabe et al. [7] and Chivavibul et al. [8,9] investigated several mechanical properties of WC–Co coatings with various Co contents fabricated by warm spray (WS) and high velocity oxy-fuel (HVOF) depositions and found the improved toughness for WC-17 and 25% Co by WS. The wear performances of WS coatings such as abrasive wear resistance were also better than those of HVOF coatings for a given hardness value. However, there still remained a substantial gap between the toughness of WS WC–Co and that of a corresponding sintered body.

Another approach to improve the mechanical properties of cermet coatings is addition of metallic phase. Osawa et al. [10] deposited a mixture of WC–20Cr_3C_2–7Ni agglomerated-sintered powder and Ni or NiCr powder by HVOF and investigated the abrasive wear and impact resistance of the coatings. The deposited coatings contained the uniformly distributed Ni or NiCr particles surrounded by WC–CrC–Ni cermet matrix. The coatings showed a significant improvement in wear and impact properties due to energy absorption by the ductile metallic particles. Hadad et al. [11] investigated adhesion strength and impact behavior of HVOF cermet coatings consisting of three layers, in which a metallic intermediate layer (Ni, Ni–Cr, Co–Cr) was sandwiched by the WC–Cr–Co layers. The intermediate layers were deposited by either HVOF or electroplating. The impact resistance of the coatings was tested by an experimental shooting device and the cermet coating with the Ni-electroplated layer exhibited better performance than the monolithic coating. The results implied the

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possibility of further enhancement of fracture properties in cermet coatings by introducing multilayer structures. Valarezo et al. [12] investigated HVOF WC–Co/stainless steel functionally graded coatings (FGC) consisting of six different layers with a stepwise change in composition from 100% stainless steel to 100% WC–Co. The FGCs exhibited high fracture resistance for vertical crackings due to energy absorption of the distributed metal phases and due to relaxation of residual stress in the coatings. In all the three cases, the essential point is adding the ductile phases in the coatings.

Based on the previous studies, the design strategy to maximize the fracture properties of WC–Co coatings can be summarized as follows. The first is to suppress the detrimental reaction during spray and the second is to add the metal reinforcements such as particles, fibers, or layers. Fiber reinforced composites [13] or laminates [14,15] are well known to have greater fracture toughness than their monolithic counterparts. Although it is of great interest to develop fiber reinforced coatings as studied in [16,17], multilayer coatings has been chosen in the present study because of the difficulty of reinforcing coatings by continuous fibers. However even for multi-layer system, since it requires rather complex operations to deposit many layers, only few works have been attempted in the past. Ravichandran et al. [18] investigated thermal conductivity of multilayer coatings of alumina and yttira-stabilized zirconia, which were deposited by plasma spraying. The maximum number of layers was 16. Although the effectiveness of multilayer structure on reduction of thermal conductivity was small, it assured the potential of thermal spray technology to make a multilayer structure. In the present paper, WC–Co/copper multilayer coatings containing 8 layers have been developed by warm spray deposition aiming at damage tolerance of cermet coatings with keeping high hardness on their surfaces. WS copper coatings showed high strength with moderate ductility in previous study [19,20] and hence copper was chosen as metal reinforcements in the current work. In order to reveal the basic and fundamental aspects of fracture characteristics of multilayer coatings deposited by warm spraying, the strength and fracture behavior of the freestanding coatings were investigated by three point bending tests.

2. Experimental procedure

Tungsten carbide–cobalt (WC–Co) and copper (Cu) layers were deposited one after the other onto a pure aluminum plate with a dimension of $50 \times 100 \times 2$ mm^3 by warm spray (WS) deposition. Powder of WC–12wt.%Co (Fujimi Inc., Aichi, Japan) with a particle size of 5–20 μm and a carbide size of 0.2 μm, and copper powder (Cu-ATW, Fukuda metal foil and powder co. ltd., Japan) with a particle size under 45 μm were used. The WC–Co powder was manufactured by spray drying and light sintering, and the copper powder was fabricated by water atomization. The aluminum substrate was chosen because it is easy to dissolve in alkali solution in order to obtain a freestanding coating.

A WS system [21] has been developed by modifying a conventional HVOF equipment (JP5000, Praxair Technology Inc., USA) by adding a mixing chamber between a combustion chamber and powder feed ports. It is capable to control temperature of combustion flame by injecting nitrogen gas at the mixing chamber so that this process can keep temperature of sprayed particles under their melting point with moderately heated and thermally softened states. The detail of the process can be found elsewhere [22]. The spraying conditions of WS process are listed in Table 1. In these conditions, both powders of WC–Co and copper were sprayed as solid states and bonded by ultra-high speed impact. Surfaces of the substrates were blasted by alumina grit and degreased by ultrasonic cleaning in acetone before spraying. Five combinations of multilayer coatings were fabricated as listed in Table 2. Samples were labeled as A, B, C, D, E in terms of Cu volume fraction, v_m = 0.0, 19.4, 31.8, 62.0, and 100.0%. The Cu volume fraction was controlled by varying the powder feed rate of Cu powder (Table 1) and thus changing their thickness ratio. Samples A and E are monolithic WC–Co and copper coatings respectively. In all cases except for sample A, the first layer on the substrate was Cu and the outer most surface was WC–Co. The total number of layers was fixed at 8 containing 4 WC–Co and 4 copper layers in all laminate samples B–D. Since the number of layers was fixed, the total thicknesses of coatings were varied among samples as shown in Table 2. After deposition of coatings, the samples were cut into rectangular bars with a dimension of 50×5 mm^2 (length × width). All the bars except for sample E were immersed into NaOH aqueous solution (NaOH: 15 g, distilled water: 500 ml) at a temperature of 60 °C, and the aluminum substrates were dissolved in order to obtain freestanding coatings. For sample E, the substrate was mechanically removed because it was very easy to obtain Cu coatings with more than 2 mm thick and thus the machining was handy for this sample.

Table 1
Spray parameter.

Parameter	Cu	WC–Co
Fuel (dm^3/min)	0.35	0.38
Oxygen (dm^3/min)	713	779
Nitrogen (dm^3/min)	1000	500
Powder feed rate (g/min)	63, 32, 16	85
Spray distance (mm)	180	
Barrel length (mm)	203.2	

Three point bending tests were conducted on those freestanding coatings. The outer span L was 40 mm and the crosshead speed of 0.1 mm/min was applied. Three specimens were tested for each case. For the cases of the multilayer coatings, the copper side surface, which was the first layer during deposition, was placed in the compression side and thus the WC–Co surface, which was the eighth layer, was placed on the tension side. The load P and crosshead displacement δ were recorded. Fracture behaviors were monitored during the bending tests by a CCD camera. The strain ε_t and the apparent bending stress σ_t on the outer most tension side for arbitrary δ were calculated as [23]

$$\varepsilon_t = \frac{6t\delta}{L^2} \tag{1}$$

$$\sigma_t = \frac{3}{2}\frac{L}{wt^2}P \tag{2}$$

where w and t is the width and thickness of the specimen. Note that σ_t is only valid for elastic deformation and cannot represent correct stress states after yielding, and thus this value should be considered as the apparent parameter. In addition, apparent work of fracture Γ was defined and calculated as the area under the load-displacement curve divided by the twice the cross section area of the specimen [24,25],

$$\Gamma = \frac{\int_0^{\delta_{max}} P d\delta}{2wt} \tag{3}$$

Table 2
Sample list.

Sample ID	Number of layer		Thickness of layer (μm)		Amount of Cu (vol. %)
	WC–Co	Cu	WC–Co	Cu	
A	1	0	600.0		0.0
B	4	4	98.9	23.7	19.4
C	4	4	93.7	43.6	31.8
D	4	4	74.0	121.0	62.0
E	0	1		1970.0	100.0