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Relationships between feedstock structure, particle parameter, coating deposition, microstructure and properties for thermally sprayed conventional and nanostructured WC–Co

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ABSTRACT

Thermal spray cermet based on tungsten carbide has been widely used due to its excellent wear resistance. The features of both carbide and binder phases are essential factors which determine the performance of cermet coating. The thermal cycling of WC–Co spray particles up to a temperature over the melting point of binder phase during thermal spraying involves the decarburization of carbide. The decarburization of carbide becomes severe with the decrease of carbide particle size, which makes it difficult yet to deposit a dense nanostructured WC–Co with a limited decarburization by thermal spraying. The decarburization not only reduces the wear-resistant phase but also leads to the formation of brittle Co–W–C ternary binder phase. Moreover, the limited decarburization involves the deposition of spray particle at a solid–liquid two-phase state with carbides at a solid state and metal binder in a molten state during spraying. High velocity impact of two-phase droplets as in high velocity oxy-fuel spraying (HVOF) results in the formation of a dense cermet coating and on the other hand leads to the possibility of rebounding of wear-resistant solid carbide particles. In this review article, the microstructural features of thermal spray WC–Co are examined based on the effect of the decarburization of tungsten carbide. The decarburization mechanisms of tungsten carbide are discussed for the control of decarburization of carbide. The effects of carbide particle size on the deposition process, adhesion of HVOF coating and wear performance of WC–Co coating as well are examined based on a solid–liquid two-phase deposition process. It is demonstrated that WC–Co cermet with different sizes of WC particles should be deposited by different processes. Moreover, the deposition of nanostructured WC–Co by thermal spraying and recent advances on the cold spraying of nanostructured WC–Co are introduced. The cold spraying with the proper design of spray powders will become promising process to deposit nanostructured WC–Co with pure cobalt binder with the hardness comparable to a sintered bulk and even high toughness of 18.9 MPa m$^{1/2}$. The pure metastable metal binder phase evolved in the deposit makes it possible to deposit hard cermet through healing the non-bonded interfaces in the coating by post-spray annealing.

1. Introduction

Cermet composites are widely used to manufacture many different wear resistant parts and tools such as miniature drills for highly integrated printed circuit boards (PCBs), pins for dot-printers, wood machining, dental work, cutting tools, rock drill tip owing to their unique combination of hardness, toughness and strength in the forms of either bulk or coatings [1,2]. Among different types of ceramic particle reinforced metal matrix cermets, carbide-containing cermet, in particular, tungsten carbide cobalt hard metals and Cr_3C_2–NiCr are mostly widely used as hard coating materials applied by thermal spray processes. The relationships between constituents, microstructure and properties for WC–Co cemented hardmetals have been well established [3]. Accordingly, the properties of cermet hardmetals, which determine their wear resistance, depend on the content of carbide and binder metal alloy, carbide size and distribution, phase structure of the alloy. Generally, with WC–Co system, the hardness of hardmetals increases with the decrease of carbide particle size and cobalt content which determines the mean free path of the binder phase, while on the contrary the toughness of the materials decreases with the decrease of carbide particle size and cobalt content [3–6]. The wear resistance of WC–Co hardmetals largely depends on their hardness and is also influenced by their toughness. When the cermet coatings are applied to wear resistant parts through thermal spray processes, the optimization of composition and microstructure is usually attempted following the fundamental knowledge established for bulk hardmetal materials.

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A thermal spray coating is deposited through the successive impact on a substrate of a stream of high velocity particles either in completely molten, half molten or completely solid state followed by deformation, rapid cooling and solidification of molten fraction. Except recently developed cold spray process, spray particles experience rapid heating to partially molten or fully molten state and subsequent rapid cooling to realize individual splat deposition. However, thermal cycling which individual spray particles experience with a maximum temperature over the melting points of the constituents in spray powder and rapid cooling during coating deposition is difficult to control, since practical spray powder particles have a wide size distribution, and temperature and velocity fields within heat sources are generally non-uniform [7,8]. Moreover, the thermal decomposition and melting of carbide, dissolution of carbide into molten metal binder phase inevitably occur [9–16]. These reactions combined with the features of spray powders and heat sources inherent to thermal spray processes bring out the difficulties for phase and composition control during WC–Co hardmetal deposition. On the other hand, the changes of phase and composition of cermet coatings with respect to the starting powder materials significantly influence the properties and performance of the resultant coatings. Therefore, many efforts have been made to establish the relationships between powder structure, processing conditions, coating microstructure and properties to optimize the performance of thermally sprayed WC–Co [14,15].

Different thermal spray processes have been employed to deposit WC–Co coating. In the fifties last century, the development of detonation gun coating process (D-gun) led to practical application of thermally sprayed WC–Co coating to aeronautic industry due to excellent adhesive strength and dense microstructure of the coating [8,17]. However, the availability of D-Gun system limited its applications. With the development and wide spreading of plasma spraying from the last sixties, WC–Co coatings were widely applied to wear resistant parts in different industries. The commercialization of HVOF (high velocity oxy-fuel) process in the early of the last eighties promoted further wide applications of WC–Co coatings with the excellent properties comparable to those of D-gun coatings [18]. No matter which thermal spray process is used to deposit WC–Co coating, the thermal cycling of spray powders exceeding the melting point of cobalt binder is involved and thermal reactions between WC and cobalt binder inevitably occur. However, with the recently emerging cold spraying process, those thermal effects are possibly avoided. WC–Co coatings can be deposited without any decarburization of carbide during spray process [19–21]. Therefore, in this review article, the emphasis is put on the microstructure evolution of WC–Co cermet coating during thermal spray deposition in the terms of high velocity solid–liquid two-phase particle impact and deposition process control during cold spraying in terms of high velocity solid particle impact, respectively.

2. Thermal effect on the microstructure of cermet coating during thermal spraying

2.1. Typical features of different thermal spray processes

The particle state parameters including structure, size, velocity and temperature prior to impact during thermal spray determine the microstructure and subsequently properties of the resultant coatings. Generally, the density of thermal spray coating is increased with the increase of spray particle velocity and temperature. Thermal reactions of WC–Co are naturally enhanced with the increase of particle temperature [14,15].

On the other hand, the parameters of spray particles are determined by the momentum and heat transfer between heat source of thermal spraying and spray particles [7,8]. Many different thermal processes including plasma spraying, detonation spraying (often referred to as D-gun process), high velocity oxy-fuel flame spraying (HVOF) and cold spraying have been used to heat and accelerate spray particles for cermet coating deposition [9–16]. It has been well understood that the highest particle velocity can be achieved by spray particles with the heat source of highest velocity of flame jet and the highest particle temperature is associated with use of heat source with the highest temperature flame jet [7,8]. Fig. 1 schematically shows the flame temperature range and achievable particle velocity range for different thermal spray heat sources. Since the maximum temperature of plasma jet reaches over 10,000 K, therefore, spray particles can be heated to a high temperature by plasma jet with a medium velocity. Although HVOF is characterized by high velocity and low flame temperature, the flame temperature is significantly influenced by type of fuel gas and flame conditions. As shown in Fig. 2 [22], the flame temperature using propane as the fuel in HOVF can reach to over 3100 K and the extensive heating of WC–Co powder may lead to the melting of a fraction of carbide. On the other hand, spray particles can be accelerated to high velocity by D-gun and HVOF processes. Moreover, the particle temperature is also influenced by its dwelling time in the flame jet and particle effective thermal conductivity. It should be noticed that the high velocity of spray particle reduces its dwelling time in the flame. Furthermore, particle size significantly influences particle heating and accelerating. Fig. 3 illustrates the effect of particle size on the change of particle velocity and temperature during in-flight along axial direction simulated for the particle with a density of 8063 kg/m^3 for HVOF torch with the dimensions schematically shown in Fig. 3c [23]. It can be recognized that the heating and accelerating rates of spray particles increase with the decrease of particle size. The small particles reach a high temperature and high velocity as well. Moreover, it has been found that the oxygen content in HVOF alloy coating increased in an exponential fashion with the decrease of spray particle size, and thus

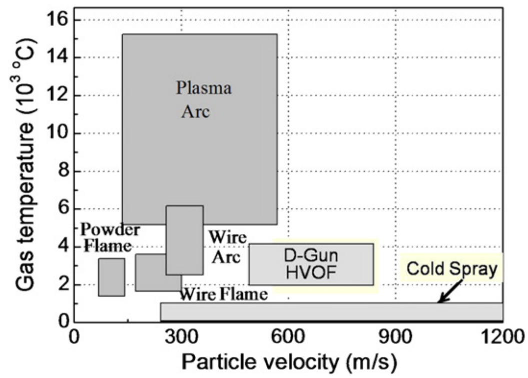

Fig. 1. Flame temperature of different thermal spray methods and obtainable particle velocity range [95].

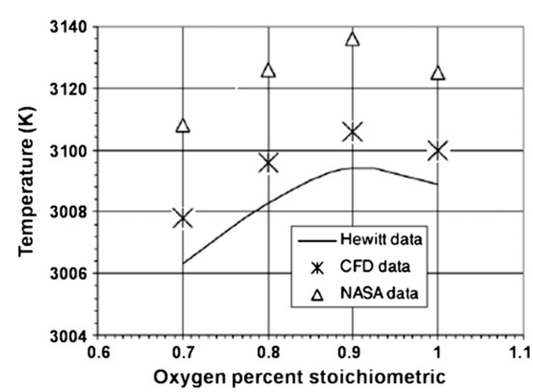

Fig. 2. WC–Co particle temperature obtained for different oxygen percent stoichiometrics for HVOF oxygen-propane flame by numerical simulation [22].