International Journal of Refractory Metals & Hard Materials 69 (2017) 138–152

Contents lists available at ScienceDirect

International Journal of Refractory Metals & Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Influence of carbide grain size and crystal characteristics on the microstructure and mechanical properties of HVOF-sprayed WC-CoCr coatings

Dafeng Wang[a,b,*], Boping Zhang[a], Chengchang Jia[a], Feng Gao[b], Yueguang Yu[b], Ke Chu[c], Mina Zhang[a], Xiaolin Zhao[a]

[a] School of Materials Science and Technology, University of Science and Technology Beijing, Beijing 100083, China
[b] Beijing General Research Institute of Mining and Metallurgy, Beijing 100160, China
[c] School of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

ARTICLE INFO

Keywords:
WC-CoCr
Carbide size
Crystal characteristics
Mechanical properties

ABSTRACT

Nanostructured WC-CoCr coatings play a significant role in industrial sectors including petrochemical and aerospace fields. However, their fracture toughness requirements still need to be further improved because of more decarburization of conventional nano scale WC grains. In the study, three representative types of WC-CoCr powders were selected to illustrate the dependence of the microstructure and mechanical properties of HVOF-sprayed coatings on the carbide grain size and their crystal characteristics in the starting powders. It is demonstrated that the ultrafine powder causes excessive decomposition of the WC phase to W_2C phase when compared to submicrostructured and nanostructured powders, owing to the WC grains with a higher density dislocation. The present study implies the critical role of apparent twin characteristics within WC grains in enhancing the microhardness and fracture toughness of the nanostructured coating. The coating deposited with nanostructured powders exhibits the best comprehensive properties, which include low decarburization, superior microhardness and fracture toughness.

1. Introduction

Such as dump valves, petroleum pipeline and landing gears, etc. equipment components that used in many industrial applications ranging from petrochemical to aerospace fields are frequently subjected to thermal cycling, abrasion, erosion and corrosion in the presence of the wear and corrosion environment [1–3]. Material degradation in service life is not only disruptive to production, but also costly to economy. For this reason, many researchers have proposed to find a protective tool for the existing materials, such as applying new types of WC-based cermet coatings. Such proposals are more economical and viable to solve component failure problem.

In the last decade, many carbide compositions such as HVOF-sprayed WC-12Co, WC-17Co and WC-10Co-4Cr are typically applied to produce dense, abrasion and erosion resistant coatings. In particular, WC-10Co-4Cr coatings are now being specified for critical applications for aircraft components such as landing gears and hydraulic rod, due to an excellent combination of wear and corrosion resistance [4]. To extend the service life of the material, it is critically desired for the production of cermet coatings with more advantageous combination of mechanical (i.e. higher hardness and toughness) and their wear resistance is made [5]. The factors influencing the mechanical properties and corresponding wear resistance of WC-based coatings have been investigated and it has been well established that the hardness, toughness, carbide grain size, phase distribution and the content of the binder phase as well as the microstructure of the coatings have great influence on the wear properties of the cermet [5–26]. Generally, decarburization of WC grains at high temperature is a well-known phenomenon especially in nanostructured WC-based coatings deposited by thermal spray. Recently, it have been demonstrated that when a decrease in WC grain size from micro-sized to nano-sized level, fine WC grains experienced more decarburization during coating preparation, leading to the enhanced hardness and reduced fracture toughness of the coating [6–15]. Ma et al. [15] compared the microstructure and mechanical properties of the HVOF-sprayed WC-12Co coatings fabricated from microstructured, submicrostructured and nanostructured powders. They observed that the WC grain size at a nanometer scale significantly increases the hardness of the coating when compared to

* Corresponding author at: School of Materials Science and Technology, University of Science and Technology Beijing, Beijing 100083, China.
E-mail address: bjing2013@hotmail.com (D. Wang).

http://dx.doi.org/10.1016/j.ijrmhm.2017.08.008
Received 20 April 2017; Received in revised form 6 August 2017; Accepted 14 August 2017
Available online 15 August 2017
0263-4368/

submicrostructured and microstructured powders, owing to the enhanced decarburization of WC grains. Nevertheless, there is still lacking a comprehensively understanding the phenomenon that the submicrostructured coating has a better performance in decarburization and fracture toughness than microstructured coating.

In addition to above results, some authors have fabricated the nanostructured WC-based coatings with higher hardness, fracture toughness and wear resistance through delicately controlling the processing conditions, as compared with the microstructured coating [16–20]. Saha et al. [16] reported a 25% increase in hardness, 35% increase in fracture toughness and a six fold increase in abrasive wear resistance of the near nanocrystalline WC-17Co HVOF coating compared to the microstructured one due to the fact that the near nanostructured WC-Co coating had a lower decarburization and greater plasticity within the coating whereas the microstructured coating suffered from significant brittle fracture, which is contradictory to the understanding that the higher surface-to-volume-ratio of WC grains generally results in more decarburization. Nonetheless, the improved performance of WC-based coating using nanostructured powders with non-optimized process parameters were also performed by many researchers [21–24]. Thakur et al. [21–23] reported that the near nanostructured WC-CoCr HVOF coating had higher hardness and fracture toughness than microstructured coating and indicated serious WC decomposition also occured in the near nanostructured coating. The result corroborated that the factors influencing the fracture toughness were closely related to not only the content of decarburized phase but also the adhesion strength between the splats. To date, works on WC-based coatings has largely been confined to be higher hardness in the nanostructured coatings than in the conventional coatings. However, there is no conclusion about whether the nanostructured WC-based HVOF coatings have higher fracture toughness compared to the conventional coatings. To the best of our knowledge, unstable performance of nanostructured WC-based coating is still one of the top challenging problems for wide applications in machinery industries besides the high cost of nano-sized raw powders. Therefore, it is necessary to investigate deeply the mechanical properties of WC-based coatings with different WC grain size so as to expand their applications.

Previous studies indicated carbides crystal characteristics played an important role in the mechanical properties of the cermet agglomerates, such as the crystal defects (i.e. dislocation and fault) and the twin within WC grains [27–29]. However, in WC-based coatings there was only one study by Stewart et al. [30], founding WC grains in the conventional WC-12Co HVOF coating were faceted with a high dislocation density whereas dislocations were little within the W_2C phase and confirming that WC grains faceted with high dislocation density were apt to decomposing to the W_2C phase having a nearly complete shell around the WC. Up to now, it is not known whether structural defects within WC grains affect the mechanical properties of WC-based coatings. As far as we know, studies related to the mechanical properties of WC-based coatings with twin characteristics have not been reported yet.

It is well known that thermally sprayed WC-based coatings exhibit complex, multi-phase microstructures, with a significantly lower volume fraction of primary carbide than that of their starting powders [1,9,30]. Various phases within coating have different microhardness such as WC phase ~2300 H_v and W_2C phase 3000 H_v [25]. How to accurately determine the relationship between the performance and the complex microstructure of the coatings remains a great challenge. A novel work on the evaluation of microhardness values under different loads of thermal sprayed WC-Co coatings by Weibull distribution analysis of identifying the individual contribution of different factors such as phase, porosity, cracks, etc. to the mechanical properties was proposed. Although several studies have investigated microhardness distribution of the WC-Co coatings and correspondingly effects on tribology properties [31–32], little work has been done on the microhardness distribution of the WC-CoCr coatings with different carbide size.

Table 1
Detailed characteristic of three WC raw material powders in this study.

Powder	WC mean size (μm)	WC grain characteristics
N	0.20	Twin
U	0.35	Apparent dislocation
S	0.86	Dislocation

To achieve the high quality coatings, the unwanted phases can be reduced by altering WC crystal characteristics. In present work, the HVOF-sprayed WC-CoCr coatings were fabricated via different structural powders, which included one type of nanostructured WC grains with twin characteristics and two types of coarse WC grains with dislocation defect characteristics. The microstructural parameters, microhardness distribution and fracture toughness of these coatings were also examined and compared with each other. The relation between microstructural features and mechanical properties are discussed both experimentally and theoretically.

2. Experimental details

2.1. Feedstock materials and coating preparation

Three types of WC-CoCr composite powders with different WC grain size and crystal characteristics were used as feedstock powders. Detailed characteristics of the WC raw material powders was presented in Table 1. These composite powders were of nominal composition WC 86 wt%-Co 10 wt%-Cr 4 wt%. For convenience, the nanostructured, ultrafine and submicronstructured WC-CoCr powders are denoted as N powders, U powders, S powders, respectively. Their corresponding coatings are denoted as N coating, U coating, S coating, respectively. The pure WC powders with three different sizes were used as raw powders in the present work. They were N WC-CoCr powder provided by Zhuzhou Cemented Carbide Group Corp. Ltd., China; Both U and S WC-CoCr powders provided by Beijing General Research Institute of Mining and Metallurgy, China. All powders were prepared via agglomerated and sintered process including [33]: (i) mechanical mixing of WC, Co and Cr powders with 3.0 wt% polyethylene glycol 6000 (as binder), 1.0 wt% polyethylene glycol 2000 (as dispersant) and 30.0 wt% distilled water to form stable slurry; (ii) spray drying to form spherical agglomerates; (iii) then the spherical agglomerates were heat-treated at 1230 °C for 8 h to consolidate the agglomerates' cohesive strength in a hydrogen atmosphere furnace. After physical crushing and air-classification, the WC-CoCr feedstock powders with typical particle size range of 15–45 μm fell within the recommended limits for HVOF thermal spraying. In the following, 'grain' will denote WC grain and 'particle' will denote agglomerates.

The substrate used for coating deposition was rectangular mild steel (ASTM 1045) with a dimension of 60 × 30 × 2.5 mm. Prior to spraying, the substrate was pre-cleaned in acetone, dried under the argon protection and then grit blasted with ~300 μm Al_2O_3 to degrease and generate sufficient surface roughness to ensure significant adhesion strength between the coating and substrate.

All the feedstock powders were sprayed onto the substrates using a GTV-K2 HVOF spray system. More details on the HVOF spraying system were introduced elsewhere [19,34]. To study the WC grain size and crystal characteristics effect on the microstructure and mechanical properties of the coatings, other influence factors should be eliminated, so all the coatings were made with the same spraying parameters. The HVOF spraying parameters were set first based on our previous studies [34], and industrially optimized coating process parameters were used for HVOF sprayed sub-micron structured coating. From these trials, online measurements of particle velocity and temperature were assisted by a DPV 2000 system (Tecnar accuraspray, Canada), to minimize the