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Fabrication of nanostructured WC–Co coating with low decarburization

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ABSTRACT

Three kinds of thermal spray powders with different densities and WC particle sizes were prepared using in-situ synthesized nanoscale WC–Co composite powder as raw material. The WC–Co coatings were then fabricated by high velocity oxy-fuel thermal spraying. The phase constitution of the as-sprayed coatings and microstructures of the feedstock particles and the coatings were analyzed. The results show that the coating prepared using powder with a relatively higher density and smaller WC particle size exhibits simultaneously lower decarburization and higher density, and further enhanced hardness. The present study suggests an effective method to fabricate nanostructured WC-based cermet coatings with high properties.

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1. Introduction

Thermal sprayed WC–Co coatings have been widely used to protect engineering components from surface abrasion/erosion in a variety of industrial environments. Nanostructuring of the cermet coating is recognized as an important approach for further improving its mechanical properties. Over the past decade, many efforts have been made to fabricate ultrafine and even nanostructured WC–Co coatings with enhanced performance as compared with conventional coarse-grained coatings [1–10].

High velocity oxy-fuel (HVOF) spraying is the most popular thermal spray technique to prepare WC–Co based coatings. However, nanoscale WC–Co powders are easily subjected to serious decarburization during HVOF thermal spraying due to their large specific surface area, leading to the decrease in the properties of the nanostructured coatings [4,5,11–13]. Moreover, achieving a dense nanostructured WC–Co coating is difficult since the nanostructured feedstock powders are usually produced by agglomeration and subsequent low temperature sintering to restrain the growth of carbide particles and hence have a porous structure [2]. Although cold-spray processing has been developed to prepare nanostructured WC–Co coatings with pure phase constitution and relatively low porosity [6], the strictly required critical conditions such as the high particle velocity and nearly vertical spraying angle strongly limit its industrial applications in the field of cermet coatings.

To overcome the shortcomings of the current processing methods, in the present study a route has been developed to fabricate nanostructured WC–Co coatings with simultaneously reduced decarburization and porosity. A comparison is made concerning the phase constitution, microstructure and hardness of the coatings prepared by our method and the studies reported in the literature.

2. Experimental

Commercially available tungsten oxide, cobalt oxide and carbon black powders were used as the raw materials. The raw powders were stoichiometrically mixed by ball milling and subsequently put in a vacuum furnace for in situ reduction and carburization reactions to prepare nanoscale WC–Co composite powder [14,15]. The 2 wt.% submicron vanadium carbide (VC) powder was added to the as-synthesized composite powder as a grain growth inhibitor. The powder was mixed with polyvinyl alcohol (PVA), polyethylene glycol (PEG) and distilled water to form a stable slurry, which was then spray-dried by a centrifugal atomizer. The spray-dried powder was heat-treated in a tubular furnace using pure argon as the protective gas. After physical grinding and air-classification, the feedstock powder with particle sizes of 10–40 μm was obtained. For comparison, the two other kinds of feedstock powders were also prepared by changing the added amount of VC and the heat-treatment temperature. The characteristics of the three feedstock powders are summarized in Table 1. The HVOF-K2 spraying system (GTV in Germany) was used to deposit the WC–Co coatings onto the carbon steel (0.45 wt.% C) substrates. The fuel flow rate, oxygen flow rate, spraying distance, powder feeding rate and carrier gas (Ar) flow rate were 24 L/h, 900 L/min, 340 mm, 98 g/min, and 7.5 L/min, respectively.

The apparent density of the feedstock powders was calculated by measuring the weight of the powder naturally stacked in a cylindrical container with the volume of 25 ml. The mean porosity of the feedstock particles was estimated by the Archimedes method. The phase constitution of the as-sprayed coatings was detected by X-ray diffraction

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Table 1
Heat-treatment conditions and characteristics of the three kinds of feedstock powders.

Feedstock powder	Composition	Heat-treatment condition	Apparent density (g/cm^3)	Mean particle porosity (vol.%)
1050H	WC–12Co	1050 °C-5 h	2.45	45.3
1200H	WC–12Co	1200 °C-5 h	4.88	11.6
VC-1200H	WC–12Co–2VC	1200 °C-5 h	4.65	13.4

(XRD, Rigaku D/max-3c) with Cu K_α radiation. For comparison, an "index of WC retention" ($I_{ret.\,WC}$) was defined as [5]: $I_{ret.WC} = I_{WC}/(I_{WC} + I_{W_2C} + I_W)$, where I_{WC}, I_{W_2C} and I_W are the intensities of the most intense X-ray diffraction peaks of the corresponding phases, respectively. The cross-sectional microstructures of the feedstock powders and coatings were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The particle size of the powder and the grain size of the coating were measured by the linear intercept method on the SEM and TEM micrographs, respectively. The porosity of the coating was estimated by the Image-Pro Plus software based on the cross-sectional SEM images at 2000× magnification in the secondary electron mode. At least five different areas were chosen for each sample to evaluate the average porosity. The microhardness tests were performed with a 300 g load and a dwell time of 15 s using a FM-700 Vickers indenter on the coating cross-section.

3. Results and discussion

Fig. 1(a) shows that the as-synthesized WC–Co composite powder has a mean particle size of 90 nm. After spray drying, the nanoscale composite powder was agglomerated into near-spherical particles. As seen in Fig. 1(b), the feedstock powder particles have a good flowability.

The cross-sectional microstructures of the agglomerated particles after the heat-treatment process are shown in Fig. 2. The agglomerated particle heat-treated at 1050 °C has the highest porosity, which is consistent with the results listed in Table 1. For the feedstock powders prepared at 1200 °C, the initial WC–Co composite particles are well compacted (see Fig. 2b and e), owing to the greater atomic diffusion at the particle–particle interface at higher temperature. With the growth of the bonding necks formed at the particle surfaces, the inner pores are gradually removed. Thus, the density of the feedstock particles prepared at the higher heat-treatment temperature was significantly increased.

Fig. 2(f) shows the energy dispersive spectroscopy (EDS) result for the individual particle of the VC-1200H feedstock powder. The detected content of V basically conforms to the original design. As compared with the two feedstock powders heat-treated at 1200 °C, the powder with the VC addition has a clearly finer WC particle size, which confirms the effect of the VC addition on the preparation of the nanostructured feedstock powder with both a high density and fine grain structure.

Fig. 3 shows the XRD patterns of the as-sprayed WC–Co coatings under the same HVOF spray conditions using different feedstock powders. Evidently, there are much more decarburized phases (W_2C and η) in the coating prepared using the feedstock having lower density. The most likely reason is that the higher porosity increases the exposure of the WC phase in the environment containing oxygen during thermal spraying, thereby resulting in less WC retained in the coating by direct oxidation reaction [4] as: $WC + O_2 \rightarrow W_2C + CO$. When the heat-treatment temperature is increased to 1200 °C, the density of the prepared feedstock powder particles is increased and hence the decarburization of the coating is significantly inhibited. There is no evident difference between the decarburization level of the two coatings prepared using the feedstock heat-treated at 1200 °C (see Fig. 3b and c). However, the WC particles in the VC-1200H feedstock are obviously finer than those in the 1200H feedstock (see Fig. 2b and e). As reported [3,16], a decrease in the WC size leads to an increase in the degree of decarburization of the coating because of the increased specific surface area of the powder particles. However, this did not occur in the present study, which reveals that the WC size has little effect on the coating decarburization when the feedstock powder particles have a higher density.

The cross-sectional microstructures of the coatings are shown in Fig. 4. The coating prepared with the VC-1200H feedstock has the lowest porosity (~0.3%). This can be understood from the formation mechanism of the pores in the coatings. Generally, two types of pores exist in sprayed coatings: one within the individual splat, and the other between the splats [4]. The former type of pores often results from the inherent voids of the powder (e.g. Fig. 2a), which cannot be completely eliminated during the HVOF spraying, as shown in Fig. 4(a) and (b). The latter type of pores depends on the flattening behavior of the thermally sprayed particles, as shown in Fig. 4(a) and (c), which is strongly influenced by the characteristics of the feedstock powder (e. g. the particle size range, the morphology and structure and the initial WC size) and spray conditions (e. g. the flame speed and temperature, the spray distance and the powder feed rate). Since the feedstock particle size range and the spray parameters were kept consistent for the fabrication of the three coatings, the difference in the coating density is likely associated with the changes in the porosity and the WC size of the feedstock powder due to the VC addition and the different heat-treatment

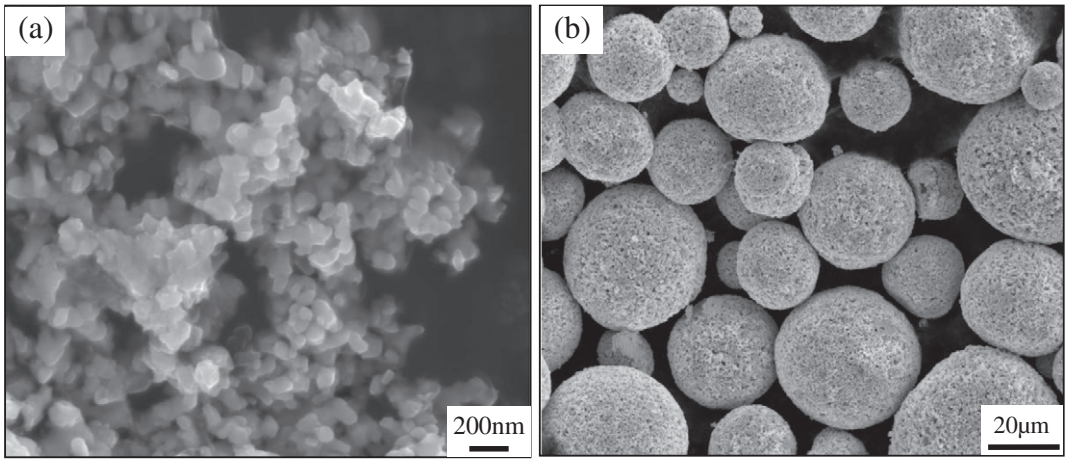

Fig. 1. Typical morphologies of (a) the as-synthesized nanoscale WC–12Co composite powder and (b) the spray-dried composite powder particles.

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