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Deposition and characterization of nanostructured WC–Co coating

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Abstract

Nanostructured WC–Co coatings were prepared with the vacuum plasma spraying process. The microstructure of the as-prepared coatings was determined with SEM, TEM and XRD. The results show that the main structure of the coatings is composed of WC grains with a mean particle size of 35 nm, which have a similar grain size to the primary powders. However, in some regions, the grain size of WC is reduced to about 10 nm due to the melting of the WC–Co powders. In some regions, WC grains are completely melted forming an amorphous phase. In some regions, WC grains have grown to 100 nm; in other regions, the second recrystallization occurred, strip-shaped and square-shaped structures are formed, which are as large as 500 nm. The main phase of the as-prepared WC–Co coating is WC with minor phases of α-W_2C, β-WC1-x, and W_3Co_3C. The hardness of the coating is about 18 Gpa with a wide distribution.

Keywords: B. Microstructure; Plasma spray; Nanostructured coating; Tungsten carbide

1. Introduction

Nanostructured ceramics exhibit novel mechanical properties [1–4], such as improved hardness, toughness and wear resistance. They have been manufactured via various methods. Thermal spray is found to be a convenient method to prepare nanostructured coatings [5–8]. Thermal spraying is a rapid process; the resident time of materials exposed to high temperature is too short to allow grains to grow extensively. In addition, thermal spraying is an economical method to deposit coatings that have extensive application in many fields such as wear resistance, corrosion resistance and oxidation resistance [9–11]. However, little work has been done to deposit nanostructured dense coating with thermal spray. In this work, nanostructured WC–Co coatings are prepared with vacuum plasma spraying.

WC–Co cermet has wide applications in machinery industries as a wear-resistance material due to the advantage in combination of hardness and toughness [12–15]. Nanostructured WC–Co cermet shows better mechanical and wear properties than conventional counterparts [4,16]. The factors influencing the wear properties have been investigated and it is reported that the hardness, toughness, carbide grain size, phase distribution and the content of the binder phase as well as the microstructure of the cermet have great influence on the wear properties of the cermet [17–19]. Previous investigations were mainly performed on conventional WC–Co coatings, little work has been done on the nanostructured WC–Co coating [20,21]. In our previous report, the tribological properties of nanostructured coatings have been investigated, it was found that nanostructured WC–Co coating showed better wear resistance than its conventional counterpart [21]. In this work, the microstructure and composition of nanostructured WC–Co coating are investigated with SEM, TEM and XRD, the microhardness of the coating is also investigated.

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2. Experimental procedure

2.1. Material preparation

Nanostructured WC–Co powders were prepared via thermochemical process including: (i) preparation of the precursor solution by dissolving ammonium metatungsnate and cobalt nitrate in water; (ii) spray drying of the precursor solution to obtain an amorphous W–Co mixture powder; and (iii) fluidized bed conversion of the amorphous W–Co precursor into nanostructured WC–Co composite. The as-prepared nanostructured WC–Co powders were then reconstituted into thermally sprayable feedstock powders via steps: (i) dispersion of nano WC–Co powders into solution; (ii) addition of binders; and (iii) spray drying of the solution in hot air. Finally, the reconstituted nano-WC–Co powders were sprayed into coatings with vacuum plasma spray equipment in an inert gas atmosphere under low-pressure condition.

A-2000 vacuum plasma spraying equipment (Sulzer Metco AG) was used to deposit nanostructured WC–Co coatings. The powders were fed with a Twin-System 10-V (Plasma-Technik AG). The plasma spraying process was carried out in an Ar gas atmosphere under a pressure of 80 mbar. The coatings were deposited onto steel substrates freshly grit-blasted before coating deposition.

2.2. Coating characterization

The surface morphology of the coatings was determined with an EPMA-8705QH22 (Shimadzu) electron probe analyzer. The coatings were polished and then analyzed with a JEM-200CX (Jeol) transmission electron microscope (TEM). The crystal structure of the coatings was measured with an RAX-10 (Rigaku) X-ray diffractometer (XRD). The hardness of WC–Co coating was determined with a Knoop indenter under a load of 100 gf. The thickness of the coating is about 0.15 mm.

3. Results and discussion

3.1. SEM of nanostructured WC–Co coating

The polished surface morphology of nanostructured WC–Co coating is presented in Fig. 1. It can be seen that the as-prepared coating possesses a dense structure with small pores well distributed in the coating. Some microcracks are also found in the coating, which are caused by the thermal stress induced in the plasma spray process.

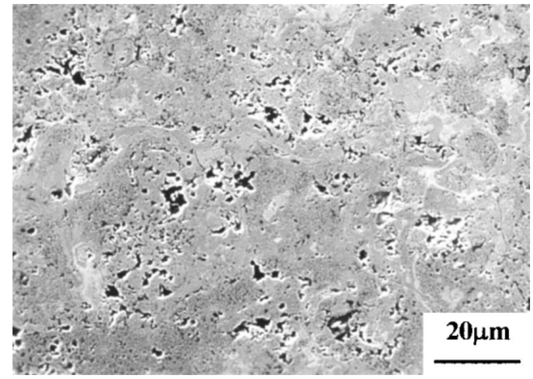

Fig. 1. SEM morphology of nanostructured WC–Co coating.

3.2. XRD of nanostructured WC–Co coating

The X-ray diffraction patterns of the nanostructured WC–Co coating and powders are presented in Fig. 2. Fig. 2(a) shows that nanostructured WC–Co powders are composed of WC and Co. Fig. 2(b) shows that nano WC–Co coating is mainly composed of WC. Minor α-W_2C, β-WC1-x, and W_3Co_3C phases are also observed in the coating as shown in Fig. 2(b). Comparing Fig. 2(a) with (b), it can be found that the diffraction intensity of Co in the coating is apparently lower than that of Co in the powders. One reason for this is that some cobalt is changed into amorphous phase, others is combined with tungsten carbide forming W_3Co_3C phase as determined by XRD analysis. Another reason is that some cobalt in the WC–Co nano powders is evaporated during vacuum plasma spray process. EDS analysis shows that the total content of cobalt in the coating is about 6.4 wt.%, which is less than that of cobalt in the powders (about 9 wt.%).

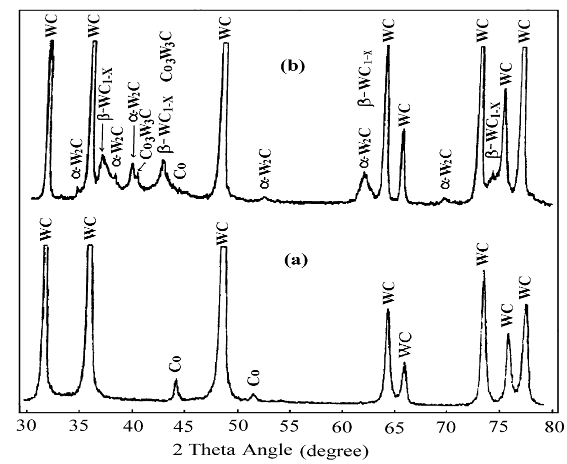

Fig. 2. XRD patterns of nanostructured WC–Co powder and coating: (a) powder; (b) coating.

3.3. TEM of nanostructured WC–Co coating

A typical structure of the plasma sprayed nanostructured WC–Co coating is presented in Fig. 3. The main structure of the coating is composed of fine grains with a mean particle size of about 35 nm. The primary particle size of WC grains in WC–Co powders is about

35 nm [22]. Apparently, the majority of WC grains do not grow during the plasma spraying process. Vacuum plasma spraying is a fast process, the velocity of plasma jet is as high as 200 ms^{-1}, the residence time of WC nano particles inside the plasma jet is less than 10^{-3} s. Thus WC nano particles are partially melted but have little time to grow up during plasma spray process. The WC particles are partially melted and highly accelerated in the plasma jet, then strike against the substrate, deform and solidify, and finally constitute the WC–Co nano coating.

Fig. 4 is the TEM morphology of a selected area of nanostructured WC–Co coating. It shows that some WC grains have a particle size of about 100 nm while others remain to be 35 nm in this region. The temperature of plasma jet was quite different at different position, with the temperature decreasing rapidly from the center to the outside [23]. The non-uniform temperature distribution in the plasma jet leads to different morphologies in the coating [7]. Powders injected into the region with higher temperature of the plasma jet, the WC grains grow more rapidly. The grain size increase is not desired in the preparation of nanostructured coating.

Fig. 5 is another selected area of nanostructured WC–Co coating. In the region, WC grains are melted in a greater degree. The particle size of WC grains is about 10 nm in diameter, which is far smaller than that of primary WC grains. Fig. 6 shows that WC grains are melted completely in some region of the plasma sprayed nanostructured WC–Co coating. In this region, amorphous phase composed of melted WC and Co is formed. These regions are formed by the completely melted WC–Co powders that are injected into the center of the plasma jet where the temperature is the highest. The complete melting of WC–Co powders is harmful to the coating, which leads to the destruction of WC grains and the formation of brittle tungsten carbides such as W_2C and W_3Co_3C.

TEM analysis shows that strip-shaped and square shaped structures are found concentrated in some regions of the nanostructured WC coating as shown in Fig. 7. SAED analysis demonstrated that these structures are WC grains [22]. Fig. 7 shows that the dimensions of these structures are quite different. The square labeled with α has a particle size of about 500 nm; the structure labeled with β is composed of two WC strips, there is a narrow intergranular phase between the two strips as indicated by γ; δ shows two parallel ultrafine WC strips with a wider intergranular phase indicated by

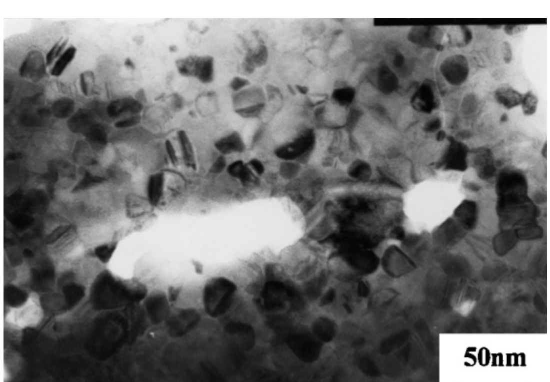

Fig. 3. TEM morphology of nanostructured WC–Co coating.

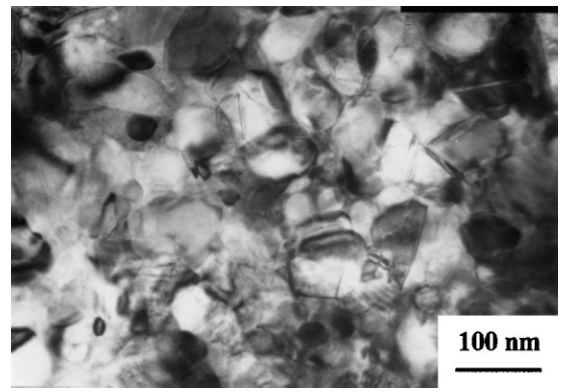

Fig. 4. TEM morphology of a selected area of nanostructured WC–Co coating.

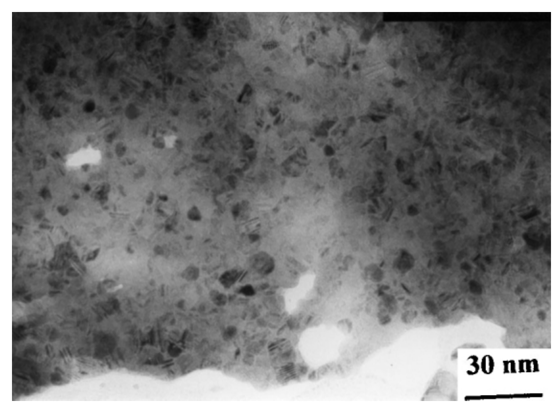

Fig. 5. TEM morphology of a selected area of nanostructured WC–Co coating.

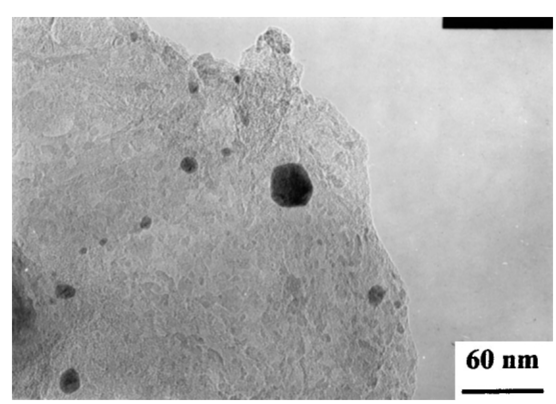

Fig. 6. TEM morphology of a selected area of nanostructured WC–Co coating.

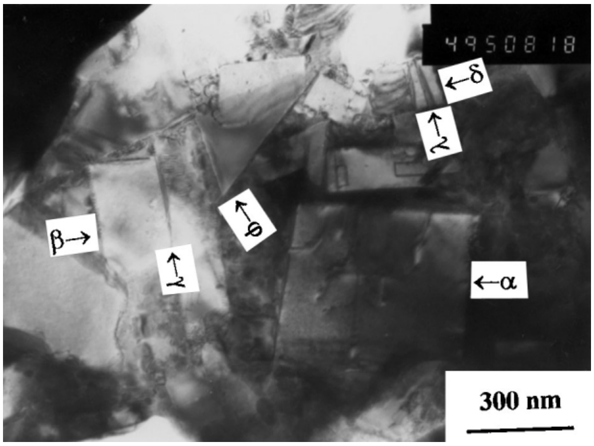

Fig. 7. TEM morphology of a selected region of nanostructured WC–Co coating.

λ. A triangular structure is also found in Fig. 7, which may be a corner of WC strip. The dimensions of these WC grains are larger than that of primary WC grains. The formation of these large grains should be due to the secondary recrystallization of WC grains during plasma spray process. The probability of nucleation of secondary recrystallization of WC grains is higher for nanostructured materials due to their fine grain size [24]. The melted interface and Co form the intergranular phase among WC grains. The structures marked as α, β and δ correspond to different stages of the secondary recrystallization. The structure marked as δ corresponds to the incipient stage; that marked as β corresponds to intermediate stage; that marked as α corresponds to the anaphase of the secondary recrystallization. HRTEM analysis shows that the square marked as α is composed of two WC strips as shown in Fig. 8. There is an intergranular layer with thickness of about 5 Å between the two grains as presented in the middle of the photograph.

On the whole, the vacuum plasma sprayed tungsten carbide coating appears as possessing a heterogeneous microstructure. This is caused by the heterogeneity of the temperature of plasma jet, with the temperature decreasing rapidly from higher than 15,000 to 1000°C from the center to the outside of the plasma jet [23]. The powders were fed into different regions of plasma jet, these in the inner flame are melted completely, these in the middle of the flame are melted partially, and these in the outer flame are melted slightly. The heterogeneous structure of the plasma sprayed coating seems to be unavoidable, however, the desired phase of the coating can be obtained as a main phase by controlling the plasma spray parameters, such as appropriate power, the spray distance, and the structure of the powders etc. As for the plasma sprayed nanostructured WC–Co coating, it is important to maintain the grain size below 100 nm in the coating in order to get a higher mechanical property.

3.4. The hardness of nanostructured WC–Co coating

The hardness distribution is illustrated in Fig. 9. Mechanical analysis shows that the hardness of nano WC–Co coating ranges from 10.1 to 25.7 GPa with a mean hardness of about 18 GPa when measured with a Knoop indenter under a load of 100 gf. According to Ref. 9 and 25, the hardness of air plasma sprayed conventional WC–Co coating is 12.3 GPa, that of vacuum plasma sprayed conventional WC–Co coating is 7.4 GPa. The hardness of nano WC–Co coating is improved comparing with that of conventional WC–Co coatings. The hardness of nano WC–Co coating seems to follow the Hall–Petch behavior of polycrystalline materials: $Hv = \sigma_0 + k_0 d^{-1/2}$, where d is the grain size and σ_0 and k_0 are experimental constants [26], i.e. the hardness increases with the decrease of the grain size. The mechanical property of nanostructured materials is different from the conventional counterpart; the grain boundary phase is here an important factor influencing the materials property [27]. The obtained hardness is the mean hardness of the intragrain component and the grain-boundary part, as the range of indentation size is about 100–140 μm which is much larger than the microstructural unit of the coating. The wide distribution of the microhardness of

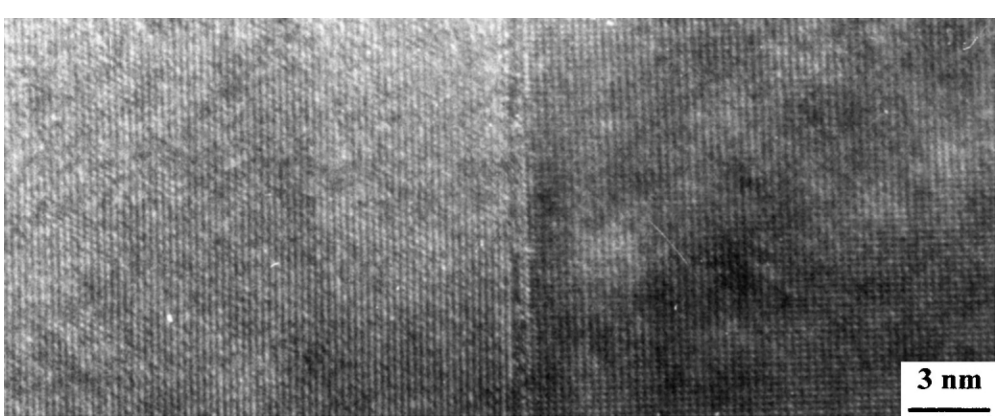

Fig. 8. HRTEM morphology of the α region of nanostructured WC–Co coating.

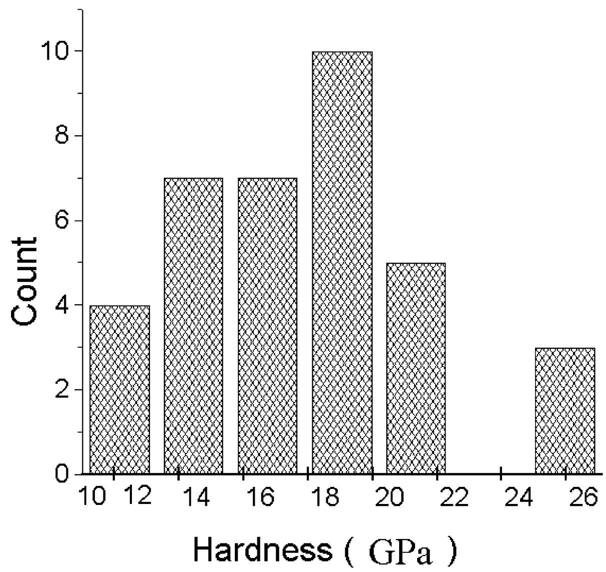

Fig. 9. Microhardness of nanostructured WC–Co coating.

nanostructured WC–Co coating is related to the variation of its microstructures. The foregoing result shows that the coating is composed of pores, WC grains with different structure and amorphous phase. The wear rate of nanostructured WC–Co coatings is lower than that of conventional WC–Co coatings due to their hardness despite of the variation of their structure [22].

4. Conclusions

The result shows that the structure of the plasma sprayed WC–Co coating is very complicated. The main structure of the coating is composed of WC grains with a mean particle size of 35 nm. In some regions, the structure is composed of WC grains with a mean particle size of 10 nm embedded in an amorphous matrix, which is formed by the melting of the WC–Co powders. Moreover, some regions of the coating are constituted completely of amorphous phase. It is also found that WC grains have grown to 100 nm in some regions of the coating. Second recrystallization occurred, strip-shaped and square shaped structures are formed in some regions of the nanostructured WC coating. The as-prepared WC–Co coating is composed mainly of WC phase with minor phases of α-W_2C, β-WC1-x, and W_3Co_3C. The hardness of nano WC–Co coating is about 18 GPa, which is apparently improved comparing with conventional WC–Co coatings.

Acknowledgements

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