Formation of Cold and Detonation Sprayed Coatings from TiB_2–Cu Nanocomposite Powders Produced by Mechanical Milling

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Abstract

Microstructure development of TiB_2–Cu nanocomposite powders during cold and detonation spraying was investigated. The powders were produced by self-propagating high-temperature synthesis (SHS) followed by mechanical milling. A computer model was developed to calculate the temperatures during detonation spraying. The change in the nanostructure of the powders during spraying was studied: due to low temperatures in cold spraying the size of TiB_2 particles in the coatings was well retained, in detonation sprayed coatings the growth of the particles was observed, the mode of spraying affecting the microstructure and the size of the particles.

INTRODUCTION

The past decade has seen the emergence of engineered coating systems developed for the next generation high-performance devices. Firstly adopted as a means to enhance the high-temperature behavior of materials, surface protection has become one of the most advanced fields of modern engineering.

The problem of electric erosion of the surface of copper parts needs to be overcome in high-current breakdown switches and rails of electromagnetic accelerators. Copper also is used in arc heater segments for heating air in industrial chambers. Electric arc causes erosion of the walls of the chamber. An effective way of protecting the walls is to coat their surface. These applications appear to warrant investigations into Cu-based erosion resistant composite materials.

Titanium diboride was proposed as a good candidate material for erosion protection possessing high electrical conductivity and refractory properties, however, the attempts made to deposit TiB_2 directly on copper substrates have been proven unsuccessful due to poor wettability of copper to TiB_2 [1]. Interfacial decohesion in TiB_2–Cu system is attributed to the fourfold difference between the thermal expansion coefficient of TiB_2 and that of Cu. Therefore, TiB_2–Cu coatings are required to overcome this problem. In our previous studies, we have shown that TiB_2–Cu nanocomposites are much more resistant to electric erosion than pure copper and their degradation proceeds through copper evaporation rather than flow

of molten droplets from the surface. The former process is more preferable for prolonged service life of the electrode [2–4]. However, synthesizing composite materials for developing desired properties is only a part of the problem: developing advanced materials for practical components can be another challenge. So, in this work, we conducted a comparative study of the microstructure of TiB_2–Cu coatings produced by cold and detonation spraying in order to find conditions for the formation of nanostructured coatings.

EXPERIMENTAL

Ti–B–Cu powders were milled and then ignited to initiate self-propagating reaction to form titanium diboride. The details of the synthesis are presented in [2, 5, 6]. The product of SHS-reaction was then mechanically milled to decrease the size of titanium diboride particles. In the final product, the size of titanium diboride particles was 50–100 nm.

As-milled nanocomposite powders were sieved. For cold spraying, composite powder particles less than 40 μm in size were separated. For detonation spraying, the powders with size (x), where $40 < x < 70$ μm, were used.

The cold spraying experiments were performed in the mode of jet impact on a substrate normally used for coating application by gas-thermal methods. In this work, air with stagnation pressure of 1.6 MPa and temperature 673 K was used as a carrier gas. The velocity of the particles was in the range of 450–580 m/s depending on the size of a particle.

The detonation coatings were obtained in three modes differing in atmosphere of spraying and particle temperature and velocities. Acetylene gas was used as a fuel. In mode 1, detonation products were reducing (the initial mixture was $C_2H_2 + O_2$). In mode 2, in order to create an oxidizing atmosphere, stoichiometric mixture $C_2H_2 + 2.5O_2$ was used so that the content of oxygen in the detonation products was 24 at. %. Composition of the detonation products in mode 3 was reducing as in mode 1, but thermal and dynamic effects on the powder were essentially raised. TiB_2–Cu powders were sprayed on a copper substrate in both methods.

The microstructure of the coatings was investigated using Field Emission Scanning Electron Microscopy (FE SEM) carried out with JSM-6500F microscope.

The samples were cross-sectioned, cold mounted, polished and etched with the solution containing $FeCl_3$. The latter was prepared using 10 g $FeCl_3 \cdot 6H_2O$, 3 ml of concentrated HCl and 100 ml of distilled water. The samples were immersed in the etching solutions for 2 min.

Vickers hardness measurements of the coatings were carried out using MVK-H1 Hardness Testing Machine. The load was 25 g.

RESULTS AND DISCUSSION

The use of blended powders for spraying composite coatings produces a microstructure with clearly different phases due to different behaviour of each type of particles during spraying process. When agglomerated/sintered powder is used, the microstructure shows a more uniform aspect suggesting that all the powder particles behave in a common way [7]. It is evident that a composite microstructure of powders to be deposited should be developed prior to spraying. The methods of mechanical milling can be useful in preparing nanocomposite powders of the uniform microstructure containing phases dramatically differing in mechanical and chemical properties. Therefore, in this work, the powders with the *in situ* developed composite microstructure were used [2].

Unlike high-temperature spraying methods, cold spraying may result in the formation of coatings at moderate and low temperatures [8]. Cold spraying, also termed cold gas dynamic spray, has emerged upon the horizon of thermal spray technology in the past few years. Typical feature of this process in comparison with the conventional thermal spray techniques is that a coating is formed by completely solid particles of low temperature and high velocity on impact. High velocity of particles (300–1200 m/s) is a principal factor determining the formation of coatings. It can be employed to produce high-quality metallic coatings without any noticeable oxidation. The low temperature characteristic also makes it possible to deposit

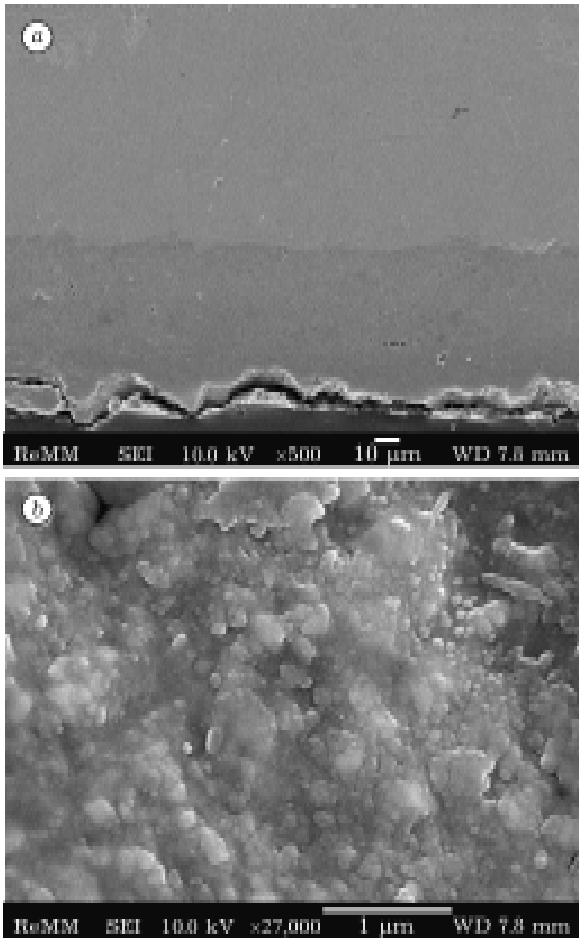

Fig. 1. General view (*a*) and microstructure (*b*) of TiB_2–43 vol. % Cu cold sprayed coating.

coatings without deteriorating the microstructure of the starting feedstocks such as nanostructured feedstocks.

Figure 1, *a* presents the evidence of dense and uniform structure of the cold sprayed TiB_2–Cu coating. It was estimated that the temperature of the particles and the substrate during the spraying did not exceed 473 K (estimated value). Due to such a low temperature, the particles did not show any increase in size during the deposition and in fact the size of titanium diboride particles was well retained (see Fig. 1, *b*).

Although far from new, the detonation spraying is widely used and studied as one of the methods of producing coatings, which are resistant to friction wear and erosion. Among the other thermal methods, detonation spraying is well known for the possibility of flexible control of gas action on a material to be deposited. The pulse principle of the process may have varying dynamic and thermal effects on particles in such a wide range that for a typical value of particle velocity 500 m/s the temperature of the particles may change from 500 to 3000 K. By varying fuel to oxidizer ratio, it is possible to change a chemical action on a material being sprayed, so that the process can be carried out in either active oxidizing or reducing atmosphere.

In this work, a computer numerical model was used [9] to calculate the temperature and velocity of particles at the time of coating formation. Dynamics of acceleration and evolution of the temperature of the powders (for the particles of the average size 55 мм) in detonation spraying are illustrated in Fig. 2, *a*, *b*, respectively. The impact velocity in mode 3 was 25 % higher than that in mode 1. The lowest impact velocity was achieved in mode 2. In mode 1, the maximum temperature of the particles of the average size reached copper melting point (see Fig. 2, *b*, curve 1). In mode 2, the thermal effect sharply increased compared to mode 1, while the dynamic action on the powder was less intense. The temperature diagram shows that in modes 2 and 3, melting of copper and heating of the melt continued in the sprayed particles (see Fig. 2, *b*, curves *2* and *3*).

Figure 3, *a*–*g* shows the SEM images of the detonation sprayed coatings. Spraying in modes

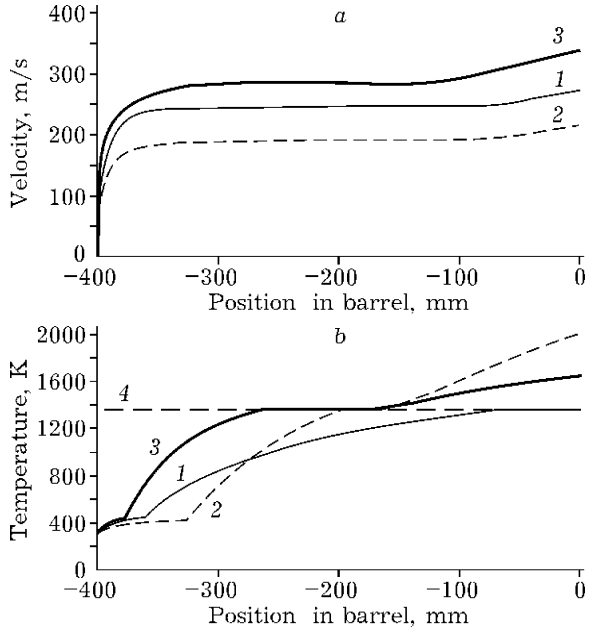

Fig. 2. Velocity (*a*) and temperature (*b*) of the particles in the barrel of the detonation gun.

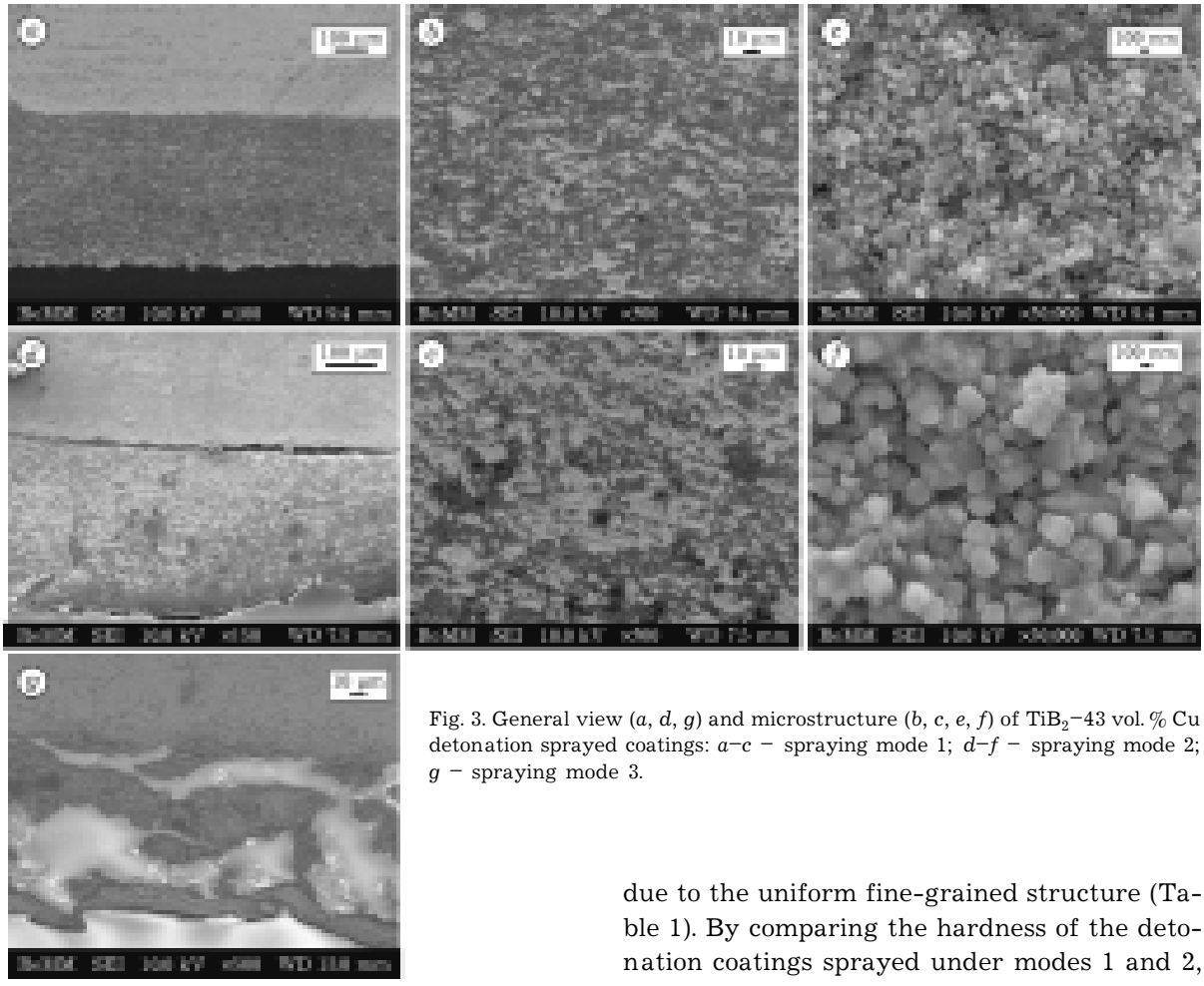

Fig. 3. General view (*a*, *d*, *g*) and microstructure (*b*, *c*, *e*, *f*) of TiB_2–43 vol. % Cu detonation sprayed coatings: *a*–*c* – spraying mode 1; *d*–*f* – spraying mode 2; *g* – spraying mode 3.

1 and 2 resulted in the formation of dense coatings of lamellar structure typical for detonation sprayed coatings (see Fig. 3, *a*, *b*, *d*, *e*). Titanium diboride particles 100–200 nm in size were observed in the coatings sprayed in mode 1 (see Fig. 3, *c*). In the case of the coatings sprayed under mode 2, well crystallized particles of titanium diboride 500 nm in size could be found (see Fig. 3, *f*). Some macrodefects were observed in the coating (see Fig. 3, *d*) due to melting of copper in the particles. So, in detonation sprayed coatings, the size of particles increased compared to that in the powders due to high temperatures involved, the mode of spraying greatly affecting the microstructure. High velocities of the molten particles in mode 3 resulted in the formation of copper pools and separation of the phases in the microstructure of the coating (see Fig. 3, *g*).

Cold sprayed coatings showed higher hardness compared to detonation sprayed coatings due to the uniform fine-grained structure (Table 1). By comparing the hardness of the detonation coatings sprayed under modes 1 and 2, it can be concluded that the growth of the particles under high-temperature conditions resulted in the decrease in the hardness of coatings.

CONCLUSION

Nanocomposite powders containing titanium diboride particles 50–100 nm in size distributed in copper matrix were deposited on a copper substrate by cold and detonation spraying techniques. The powders were produced by self-propagating high-temperature synthesis (SHS), followed by mechanical milling.

TABLE 1

Hardness of TiB_2–43 vol. % Cu coatings

Spraying technique	Vickers hardness
Cold	378
Detonation (mode 1)	332
Detonation (mode 2)	270

Microstructure of the coatings was studied in order to evaluate the possibility of nanostructure retention of the powders in the coating layers. Cold sprayed TiB_2–Cu coatings were dense and uniform, and the size of titanium diboride was well retained. In the case of detonation sprayed coatings, the size of the particles grew compared to that in the powders and the coatings exhibited particular lamellar structure. Depending on the mode of detonation spraying, 100–200 and 500 nm well crystallized particles of TiB_2 were found in the coatings. When the temperature and velocity of the particles in detonation spraying were increased, copper pools and non-uniformities formed in the microstructure. Cold sprayed coatings showed higher hardness compared to detonation sprayed coatings.

In the development of this research, TiB_2–Cu nanocomposite coatings of different phase ratio are being tested for resistance to electric erosion and the results of these studies will be reported elsewhere.

Acknowledgements

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