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Ti-B-C Composite Coating Produced by Electrothermally Exploded Powder-Spray Technique

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Composite coatings of a Ti-B-C system were reactively produced by the electrothermally exploded powder-spray (ELTEPS) technique. First, the electrical characteristics of the ELTEPS system were determined. The starting powder of the coatings was titanium powder mixed with boron carbide powder. This powder was prepared for production of Ti-B-C composite coatings on substrates using the ELTEPS technique. The coatings obtained were composed of titanium carbide and titanium diboride. The thickness of the coating obtained by onefold spray was not uniform. The coating obtained by the twofold spray covered the substrate. The coating obtained by threefold spray was still more precise. The thickness of the coating obtained by threefold spray was about 50 µm, and its hardness value was about 30.7 ± 4.5 GPa.

Keywords composite materials, electrothermal explosion technique, nanocrystalline composites

1. Introduction

Due to rapid advances in technology in recent years, industrial machines are being used in more extreme environments, and thus the development of materials that can withstand such severe environments is desired. In the performance of material, the surface that comes into contact with the outside environment occupies an important position. To develop materials that can endure such severe environments without failing, a variety of surface treatment technologies have been developed.

Spray technology has attracted attention from various fields. Spray technology expands the variety of materials that can be used, and thick coatings can be formed at high coating speeds.

Moreover, a coating that adheres well to the substrate is also required. For this reason, the ceramic coating process from a thermal spray consists of two layers: a topcoat of ceramic and an undercoat of metal. With the undercoat, the adhesion becomes stronger and the heat stress between the ceramics and the substrate is reduced.

However, even when an undercoat is applied, the fact that the interfaces between the ceramics and the undercoat are the main weakness must be taken into account. Heat stress concentration takes place between ceramics and an undercoat due to differences in heat characteristics.

Therefore, improvement of coating is required to reduce heat stress concentration. One method for attenuating heat stress concentration is to change the organization of the interface in a gradient fashion. Hence, development of coating that consists of graded layers was taken into consideration for the reduction of heat stress.

In such methods, the amount of supply of ceramics and undercoat metal powder is controlled, and a graded layer is produced. The supply control, however, is a complex procedure.

The electrothermally exploded powder-spray (ELTEPS) technique differs from such methods. With the ELTEPS technique, it is possible to produce coatings with a graded layer composed of a mixture of ceramics and substrate metals simply by spraying ceramic powders (Ref 1, 2).

Moreover, the ELTEPS technique allows one to increase and decrease the volume of starting material, and material composition can be regulated easily. ELTEPS uses only electric power, so changing the volume of spray energy is easy. Moreover, the application of chemical reactions to ELTEPS can produce a nanocrystalline coating (Ref 1).

Titanium carbide (TiC) and titanium diboride (TiB_2) are of great interest as spray materials. Titanium carbide has high wear-resistance and hardness as well as a high melting point. Titanium diboride has a low density, is hard, and has a high melting point. It is thought that the ductility, which is a weak point of TiB_2, could be augmented with the addition of TiC. Therefore, titanium carbide/titanium boride composites hold great promise for applications as high-temperature structural components, as wear resistant elements, and so on (Ref 3-11).

The objective of the current study was to synthesize a Ti-B-C composite coating using reactive ELTEPS. This study is a preliminary step in a research project with the goal of using ELTEPS to create a boride composite coating with high ductility.

2. Experimental Setup

2.1 ELTEPS Equipment

Figure 1 shows the electrical circuit for the electrothermal explosion of powders and the signal network. The ELTEPS process is performed with an electric circuit consisting of a large

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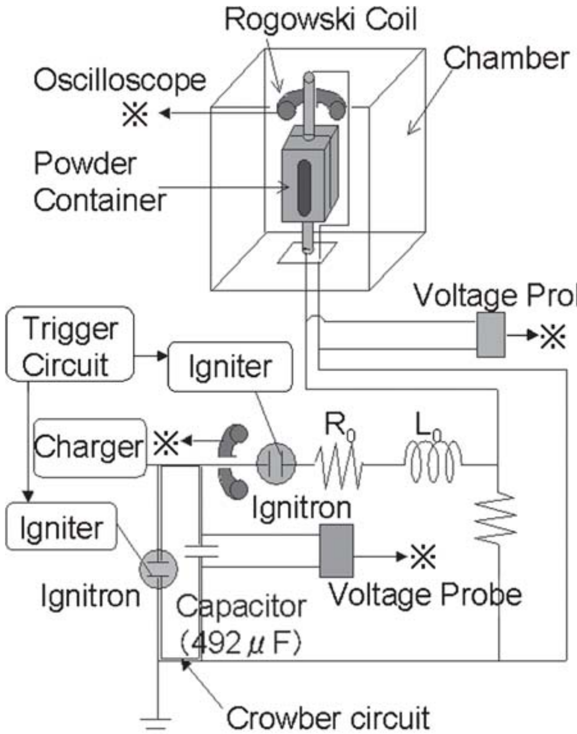


Fig. 1 Experimental setup for ELTEPS

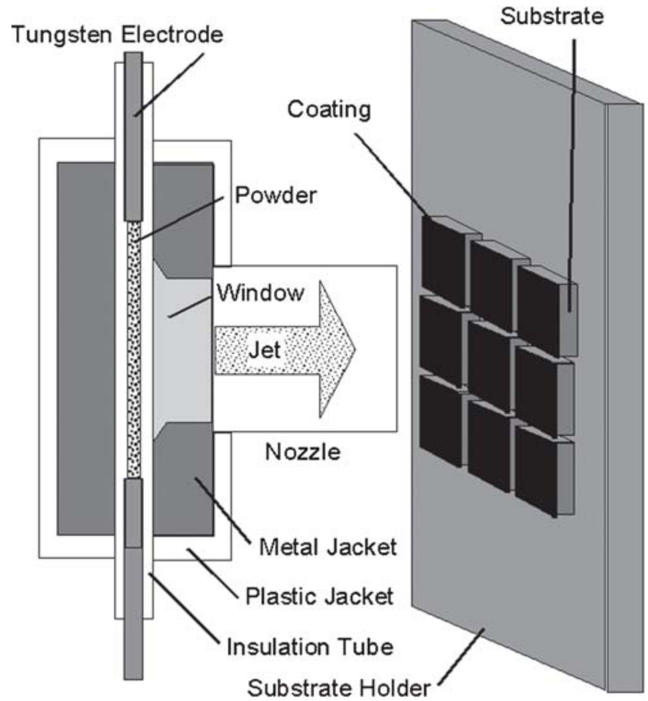


Fig. 2 Schematic cross section of a powder container

capacitor and a vacuum chamber in which a powder is installed between a pair of electrical contacts. The powder is charged in the container. The container consists of a polyethylene tube charged with starting powder, a metal jacket, and an insulation jacket. The jacket has a window that faces the substrate holder.

Figure 2 shows a schematic of a sectioned powder container. The sample container consists of an electric insulation pipe (polyethylene tube), a metal jacket (SNCM), tungsten electrodes, and a plastic jacket (polycarbonate) for electric insulation. A polyethylene tube was filled with the sample under an argon atmosphere, and both ends of the tubes were closed with the tungsten electrodes using epoxy resin. The polyethylene tube filled with the sample was attached to a metal jacket to which a window for the spray was attached, and for electric insulation the metal jacket was covered with a plastic jacket.

The capacitor supplied high voltages and high currents through the electrical contact to the powder.

Molten particles produced by Joule heating were ejected from the tube through the jacket window during an electrothermal explosion. To guide the spray jet coming from the window, a metal nozzle was installed in the container (Ref 2). The molten particles were sprayed on the substrate in the shape of the tile already installed on the substrate holder located at a distance of 172.5 mm from the container axis.

2.2 Powder Preparation and Spray Conditions

Substrates used were mild steels on which a Ni-20% Cr coating was plasma sprayed as an undercoat.

The starting powder was a mechanically mixed powder of Ti (Sumitomo Sitix Co., Tokyo, Japan; particle size, <150 μm; purity, 99.8%) and B_4C (Kojundo Chemical Laboratory Co., Sakato, Japan; particle size, <10 μm; purity, 99.9%). Ti is an electrical conductor. Moreover, B_4C is an insulator. Therefore, the sizes of the Ti and B_4C powders were changed. It is thought that Ti, to which electricity flows preferentially, is heated, the heat is transferred across to B_4C, and B_4C is melted. Therefore, before B_4C is subject to heat and melts, in order for Ti to evaporate and to prevent explosion, the size of the powder of Ti was enlarged.

The mixing was performed in a V-shaped blender for 24 h. The molar ratio of Ti to B_4C in the former powder was chosen to allow the following chemical reaction:

$$3Ti + B_4C \rightarrow 2TiB_2 + TiC$$

Figure 3 shows scanning electron microscopy (SEM) images of starting powder and surface of substrate. The starting powder was charged in a polyethylene tube at a relative density of ~55% under argon gas at atmospheric pressure. The spray chamber was filled with nitrogen gas at about 13.3 kPa prior to spraying. The Joule heat was estimated by measuring the voltage and current applied to the powder (Ref 1, 12).

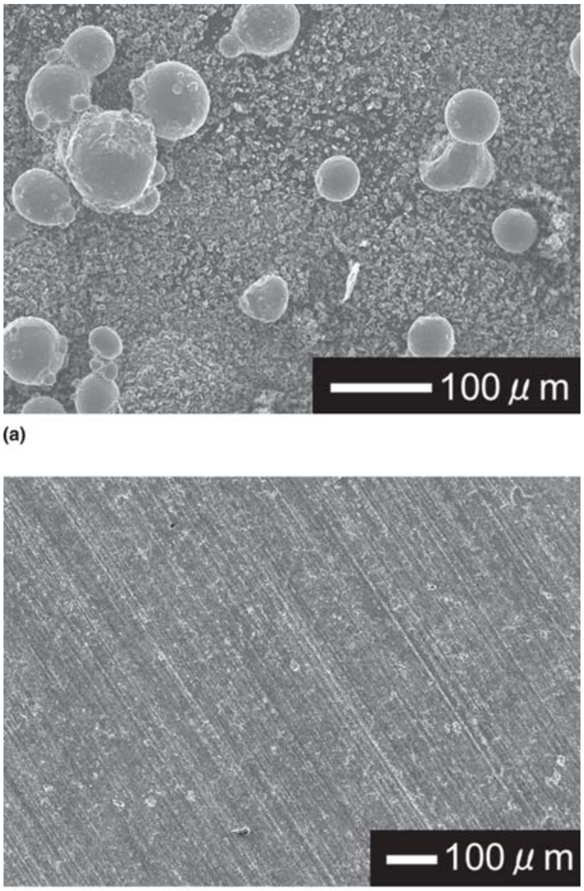
In this work, spraying was performed not just once, but two or more times.

The energy supplied to the sample in all experiments was about 10.6 kJ/g.

2.3 Coating Characteristics

To investigate the properties of the coating that was obtained, the following analytical equipment was used. Before analysis, the obtained coating was washed in acetone using an ultrasonic washing machine.

The structural crystal phases of the coatings were identified with an x-ray diffractometer (XRD, Model Rint-2000, Rigaku Denki Co., Tokyo, Japan) using Cu Kα radiation.



(a)

(b)

Fig. 3 SEM image of (a) starting powder and (b) surface of substrate before spray coating

A morphology of cross sections of the coatings was characterized with a scanning electron microscope (SEM, Model JSM-5310, JEOL Co., Akishima, Japan).

The Vickers microhardness of the coating was measured with a hardness tester (Model MVK-EIII, Akashi Co., Tokyo, Japan). Ten indents were made to determine the hardness of various areas in the coatings.

Constituent elements of the coatings were analyzed with an electron probe microanalyzer (EPMA, Model EPMA-1400, Shimadzu Co., Kyoto, Japan).

3. Results and Discussion

Initially, the spray was applied one time only at a distance of 100 mm, with the expectation that an even and precise Ti-B-C compound coating would result. However, the coating obtained contained numerous pores and cracks, although a thickness of about 40 μm was achieved. Thus, to produce an even and precise coating, the spray was applied two or three times. Although the thickness of the coating was increased and the number of pores and cracks was reduced, damage to the Ni-20% Cr substrate layer was intense. This was probably due to the fact that the weight of the Ti is light while the speed of the molten particles that collide with the substrate is fast.

Therefore, to reduce the speed of the molten particles and thereby soften their collision with the substrate, the distance of the spray was extended to 172.5 mm and the spray was performed.

Results of analysis of the coating obtained from 172.5 mm are shown below.

Figure 4 shows SEM images of the coating surface under different numbers of sprays.

Polishing marks were observed before spraying the substrate, but none was seen on the substrate after the onefold spray. In addition, the form of substrate after the onefold spray was not confirmed, but spread was observed. For this reason, it is thought that the sample was melted and was deposited on the substrate.

Many cracks are shown on the surface of the onefold spray coating, and the surface of the coating is very uneven. The number of cracks (the widths of which were about 2 μm) per 0.1 mm^2 observable by SEM was 3.1. Compared with the coating surface after carrying out a onefold spray, the crack of the coating surface after carrying out a twofold spray decreased, and the unevenness was also reduced. The number of cracks (the widths of which were about 2 μm) per 0.1 mm^2 observable by SEM was 1.8 after a twofold spray. Moreover, cracking decreased compared with the coating surface after carrying out a twofold spray and further decreased after carrying out a threefold spray. Unevenness likewise decreased. The number of cracks (the widths of which were about 2 μm) per 0.1 mm^2 observable by SEM was 0.2 after the threefold spray.

Because the location of the coating surface after a onefold spray to which molten particles adhered was uneven, the unevenness on the surface of the coating was great. However, the unevenness of the location where molten particles adhered by multifold sprays was lessened, resulting in a comparatively flat coating surface.

Moreover, in a onefold spray, much cracking occurred on the coating surface. It was thought that the cause of the cracking was the difference in characteristics of the substrate surface and coating. However, the multifold sprays are sprayed onto a coating that is already compounded by a onefold spray. Therefore, the difference in properties of the substrate surface and coating is eased. Cracking is thought to decrease as a result.

For this reason, in ELTEPS, it is thought that multifold spray has an effect in compounding coating.

Figure 5 shows the XRD pattern of the starting powder the surfaces of the coatings resulting from different numbers of sprays.

Ti and B_4C peaks were observed in the starting powder but not in the coating. TiC and TiB_2 peaks were observed in the coating instead, indicating that a chemical reaction had occurred. Moreover, a Ni peak was observed in the XRD analysis on the surface of the coating after carrying out a onefold spray. Because nickel is the substrate, it is thought that the substrate was not completely covered by the coating. A part of the substrate had appeared on the surface. However, in XRD analysis of the surface of the coating after carrying out a twofold spray, as the peak of the nickel was not observed after carrying out a twofold spray, the substrate is thought to be completely covered by the coating. This tendency did not change in the threefold spray either.

In the threefold spray, the intensity of TiC and TiB_2 increased

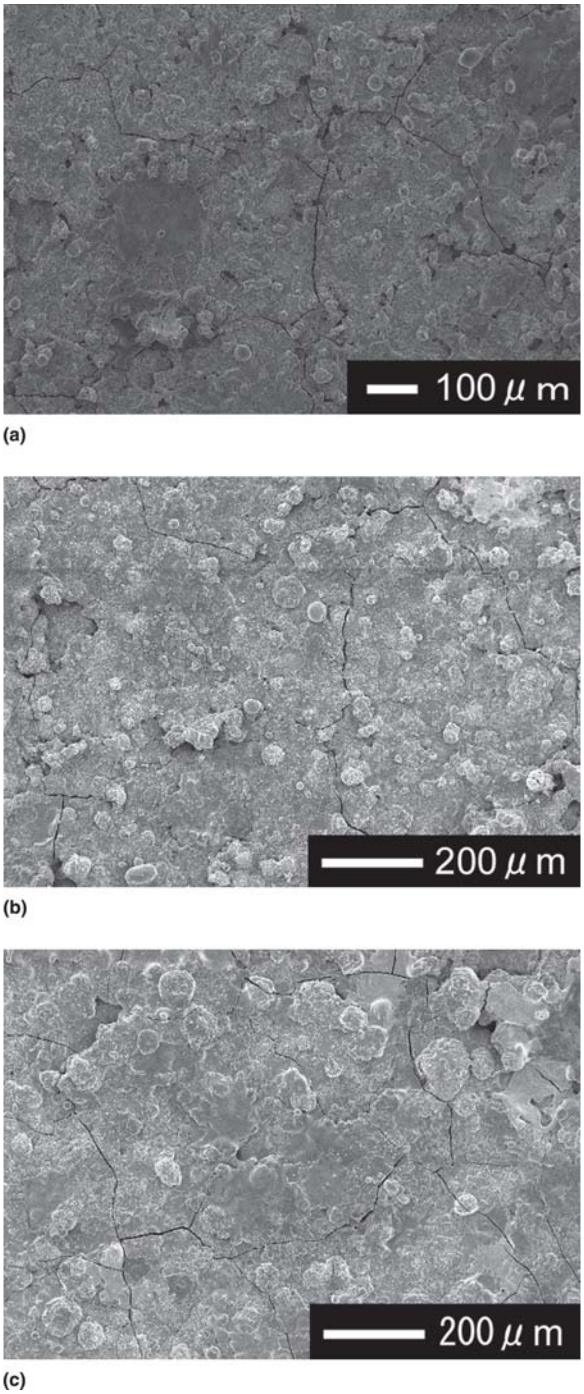


Fig. 4 SEM image of (a) surface of sprayed coating, (b) surface of twofold sprayed coating, and (c) surface of threefold sprayed coating

compared with the onefold spray, and the growth of the coating is thought to progress in the same manner as the twofold spray. Even when the substrate was sprayed many times, the materials that constituted the coating were TiC and TiB_2. For this reason, it was concluded that starting powder was mixed to an extent sufficient to synthesize the coating.

Figure 6 shows SEM images of cross sections of a coating under different numbers of sprays. A part of the substrate after

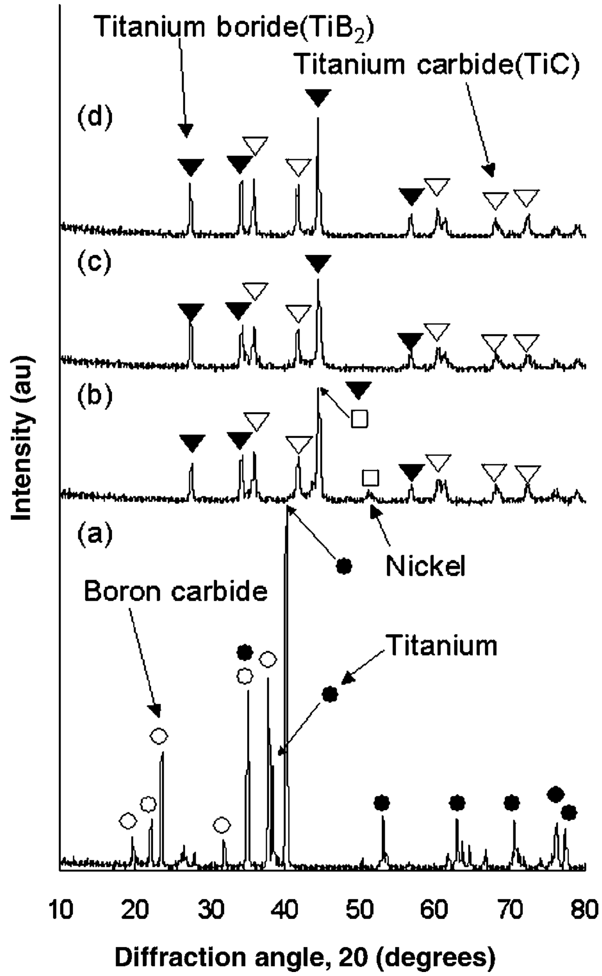


Fig. 5 XRD patterns of (a) starting powder, (b) onefold sprayed coating surface, (c) twofold sprayed coating surface, and (d) threefold sprayed coating

carrying out a onefold spray was not covered by the coating, and the substrate after carrying out a twofold spray was covered by the coating. These results correspond to XRD analysis.

The substrate was not covered uniformly, and in the coating there were large pores and many cracks, confirmed by Fig. 6(a). The coating was about 40 μm at its thickest place.

In Fig. 6(b), the thickness of the coating became uniform, and the number of the cracks in the coating and the size of pores had decreased. The thickness of the obtained coating was 40 μm on average. It is thought that the coating obtained by the twofold spray became smooth because the particles produced by the twofold spray went into the cracks of coating obtained by the onefold spray.

In Fig. 6(c), the cracking in the coating and the number of pores decreased, and the coating became even smoother.

Graded layers in which the coating and substrate are mixed at the coating interface were not observed. This was also confirmed from the results of element mapping of the substrate material in EPMA. Because it has been confirmed that the coating substances are mixed at a distance of 100 mm, it was determined that the reason it had not mixed was the spraying distance. Thus,

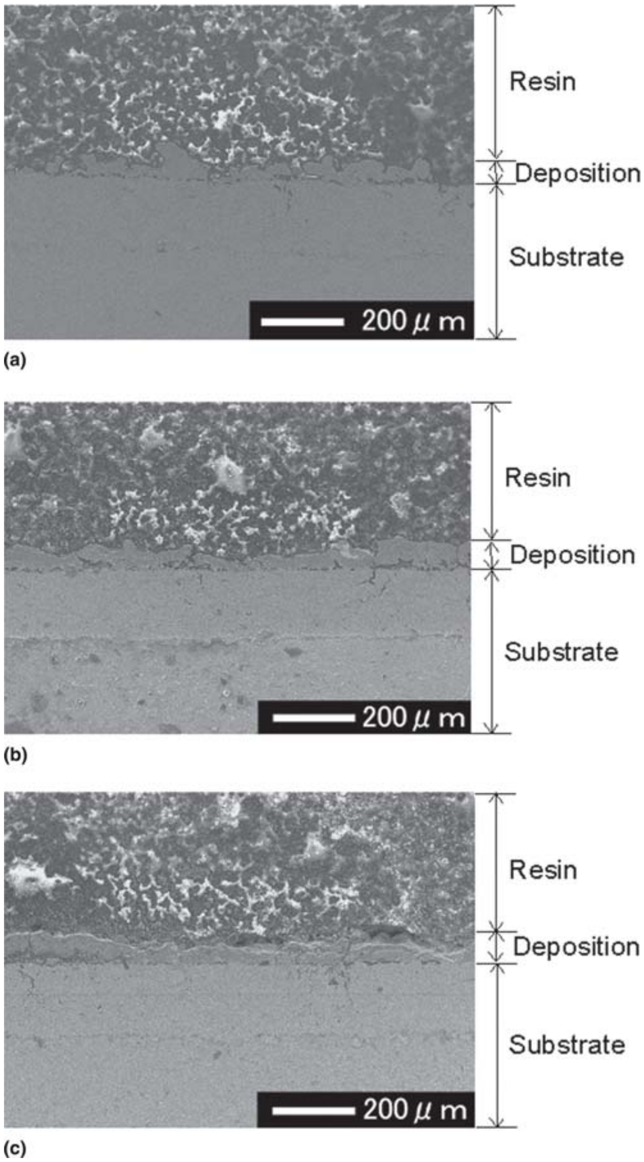


Fig. 6 SEM image of cross section of (a) onefold sprayed coating, (b) twofold sprayed coating, and (c) threefold sprayed coating

because the coating and the substrate did not mix, it is thought that the adhesion power would be small.

The hardness of the coating obtained by a threefold spray was then measured. The value of obtained hardness was 30.7 ± 4.5 GPa. This value was larger than the value of TiC and showed a value near TiB_2. That the main constituent is TiB_2 can also be confirmed using this value and the assumed reaction formula.

From the results above, it is thought that a multifold spray is effective in the composition of a Ti-B-C compound coating. It was observed in the SEM image that the threefold sprayed coating covers the substrate.

In this study, the authors were successful in producing a coating of Ti-B-C that consisted of TiB_2 and TiC by the ELTEPS technique. Furthermore, it is thought that a coating that can also be used industrially could be produced by improving spray conditions, etc.

4. Conclusions

Ti-B-C composite multifold-sprayed coatings were produced by the ELTEPS technique by use of a starting powder composed of a mixture of Ti and B_4C particles. Substrates used were mild steels on which Ni-20% Cr was plasma-sprayed as an undercoat to 200 μm thickness. The composition and microstructure of the coatings obtained were examined.

There were also many cracks, and the unevenness of the surface of the coating obtained by a onefold spray was large. On the surface of the coating obtained by a threefold spray, the cracking and unevenness decreased.

In XRD analysis of the surface of the coating obtained by a onefold spray, peaks corresponding to TiC and TiB_2 were observed whereas Ti and B_4C peaks were not. Moreover, the peak of Ni, which is the substance of the substrate, was also observed. In the XRD analysis of the surface of the coating obtained by the twofold spray, only the peaks of TiC and TiB_2 were observed, with no observable Ni peak.

The coating obtained by onefold spray was not uniform, and although the coating did not cover some of the substrate, the coating obtained by the twofold spray did cover the substrate. The coating obtained by threefold spray was even smoother. The thickness of the coating obtained by threefold spray was about 50 μm, and the value of hardness was ~30.7 ± 4.5 GPa.

The purpose of the experiment was to confirm if such a coating could be synthesized. A large-sized sample was not produced. Other characteristics, such as adhesion, could not be investigated for such reasons. In the future we plan to increase the size of the sample to investigate such characteristics.

Moreover, in this study, mixture of the coating with the substrate substance at the interface between the coating and substrate could not be observed. For these reasons, future research will include an increase in the spray distance (to ~150 mm). The authors also intend to measure other characteristics.

In future research, spraying will be performed using other systems to investigate whether they would produce results similar to those obtained in the current study, and to apply this spray method to other materials.

References

1. H. Tamura, F.G. Wei, and T. Kodama, TiN-TiB_2 Composite Coatings Reactively Produced by Electrothermally Exploded Powder Spray, *J. Therm. Spray Technol.,* 2002, 11 (1), p 100-106
2. T. Kodama, Y. Ikeda, and H. Tamura, *J. Therm. Spray Technol.,* 1999, 8 (4), p 537-544
3. D. Brodkin, A. Zavaliangos, S.R. Kalidindi, and M.W. Barsoum, *J. Am. Ceram. Soc.,* 1999, 82 (3), p 665-672
4. G. Wen, S.B. Li, B.S. Zhang, and Z.X. Guo, *Acta Mater.,* 2001, 49, p 1463-1470
5. W. Wang, Z. Fu, H. Wang, and R. Yuan, *J. Eur. Ceram. Soc.,* 2002, 22, p 1045-1049
6. S.K. Bhaumik, C. Divakar, A.K. Singh, and G.S. Upadhyaya, *Mater. Sci. Eng.,* 2000, A279, p 275-281
7. H. Zhao and Y.-B. Cheng, *Ceram. Int.,* 1999, 25, p 353-358
8. I.E. Degrave, A. Zavaliangos, S.R. Kalidindi, and M.W. Barsoum, *Mater. Sci. Eng.,* 2000, A279, p 275-281
9. S. Rodriguez, V.B. Munoz, V. Esquivel, and L.E. Murr, *J. Mater. Sci. Lett.,* 2002, 21, p 1661-1666
10. C. Mitter, P.H. Mayrhofer, et al., *Surf. Coat. Technol.,* 1999, 120-121, p 405-411
11. A. Kulpa and T. Troczynski, *J. Am. Ceram. Soc.,* 1996, 79 (2), p 518-520
12. Y. Ikeda, H. Tamura, and A.B. Sawaoka, *Rev. High Pressure Sci. Technol.,* 1998, 7, p 1472-1474