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Copper-Titanium Diboride Coatings Obtained by Plasma Spraying Reactive Micropellets

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Electrotribological applications require materials with both high electrical conductivity and wear resistance. For this purpose, a copper-base plasma sprayed coating containing titanium diboride particles was developed. The process for fabricating this Cu-TiB_2 coating consists of plasma spraying reactive powders that contain a Cu-Ti alloy and boron. The reaction between the copper alloy and boron proceeds in different steps going from solid-state diffusion of titanium and copper to the synthesis of TiB_2 in a liquid below 1083 °C. Plasma sprayed copper coatings contain finer TiB_2 crystals than Cu-TiB_2 materials synthesized in a furnace at 1200 °C. Coatings with 25 vol% TiB_2 have hardnesses that are comparable to Cu-Co-Be and Cu-Ni-Be alloys and to Cu-W and Cu-Mo alloys used in spot welding. Their low electrical resistivity of 52 $\mu\Omega \cdot$ cm could be increased by lowering the oxygen content with coatings and controlling the formation of TiB_2 clusters, the titanium content in solution in copper remaining low after the synthesis reaction.

1. Introduction

In electrotribological applications, high-conductivity copper cannot be directly used because it is soft, and therefore, its mechanical properties must be increased to withstand severe attacks. Numerous methods can be used to toughen and strengthen copper such as alloying or precipitation hardening. Copper also can be strengthened by the addition of phases such as oxides or metals and graphite may be used to increase sliding properties. The reinforcing phases can be introduced into copper or formed *in situ*. An example of the latter technique is the internal oxidation of a metal inclusion.

Previous work has shown the possibility of synthesizing a ceramic phase by the *in situ* reaction of elements dissolved in a metallic bath.[1] The principle governing the direct formation of TiB_2 within a ferrous matrix was successfully applied to the plasma spraying of reactive materials.[2] It was also shown recently that titanium diboride can be formed within titanium-copper alloys or mixtures of copper and titanium with the addition of elemental boron.[3] The present work was aimed at assessing the fabrication of plasma sprayed copper coatings containing dispersed TiB_2 particles formed upon spraying and in evaluating their properties for electrotribological applications.

Key Words: copper titanium-diboride coatings, electrotribological, microstructural properties, plasma spray, reactive spraying

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2. Experimental Procedure and Materials

Commercial titanium bronze and amorphous boron powders were used as the starting materials for the preparation of Cu-TiB_2 composite materials. The chemical analysis of these as-received powders is given in Table 1. The 10 wt% titanium bronze was mixed with boron in a stoichiometric proportion to form TiB_2. After the complete transformation of titanium into titanium diboride, the composite material is expected to contain 13.9 wt% or 24.4 vol% titanium diboride. X-ray diffraction analysis showed that the as-received 10 wt% titanium bronze powder consists of Cu, Ti, Cu_4Ti, and Cu_4Ti_3. Differential thermal analysis (DTA) was used to determine the reaction temperature between titanium bronze and boron. Tests were carried out in argon atmosphere at a heating rate of 10 °C s^{-1}.

For the fabrication of composite spray powders containing titanium bronze and boron, the starting titanium bronze powder was ground in isopropanol with a high-speed attrition mill using tungsten carbide balls. After 10 h of attrition milling, the fine boron powder (typical particle size, 1 μm) was added to the slurry with the appropriate quantity of a dispersing agent. The resulting powder mixture was very reactive after drying. For forming spray powders, the powder mixture was agglomerated using a proprietary process that avoids excessive heating and maintains the process temperature below 60 °C. At the end of the agglomeration process and after sieving, a fine (+38 −75 μm) spray powder was obtained, as shown in Fig. 1. These reactive micropellets were plasma sprayed in atmospheric air on ceramic and metallic substrates using a commercial spraying system with the spray parameters listed in Table 2.

For comparison purposes, 5-g test coupons made of compacted powders were heated for 1 h to 1200 °C under flowing ar-

Table 1 Chemical analysis of materials

	Composition, wt%							
Material	**B**	**Si**	**Mg**	**Fe**	**Ca**	**O**	**Cu**	**Ti**
Boron	95-97	0.3	0.2	0.1	0.1	Bal	...	...
Titanium bronze	Impurity, 1% max					...	90	10

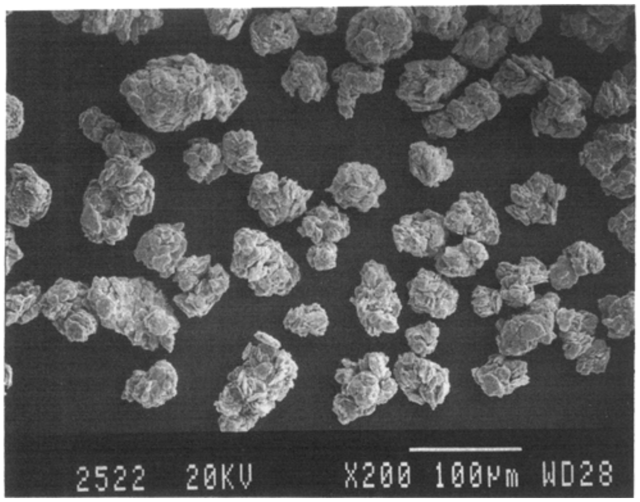

Fig. 1 Typical morphology of agglomerated powders containing 10 wt% titanium bronze and boron.

Table 2 Plasma spraying parameters

Parameters	Conditions
Arc gas	Argon-helium (63 vol%)
Torch	Bay-State Abrasive #PG-120
Gas flow rate, (L/s)	2.8-3.0
Arc current, A	500
Arc voltage, V	50
Powder carrier gas	Argon
Gas flow rate, L/s	0.03
Spray rate, g//min	4.2
Deposition efficiency, %	62

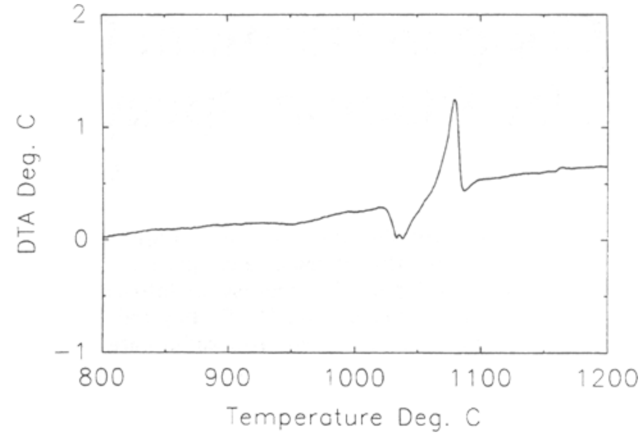

Fig. 2 Differential thermal analysis of a mixture comprising 10 wt% titanium bronze and boron. Boron to titanium atomic ratio is 2.

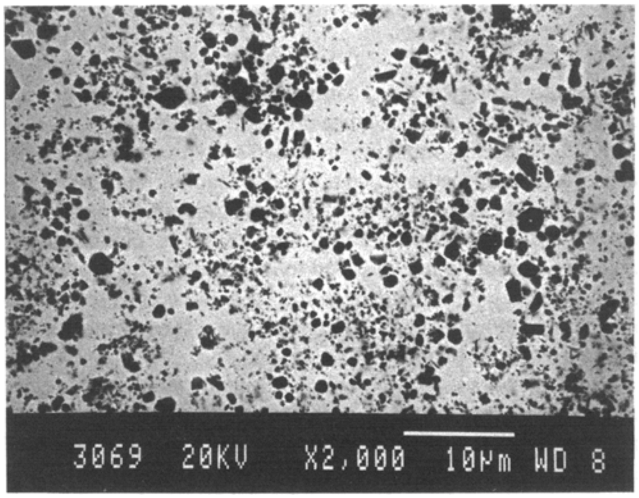

Fig. 3 Backscattered scanning electron micrograph of the Cu-TiB_2 composite obtained after furnace melting. The approximately equiaxed dark phase is TiB_2.

gon at a pressure of 65 kPa in an electric resistance furnace. Metallographic cross sections of compacts and sprayed coatings were observed by optical and scanning electron microscopy. Microhardness measurements were performed with a Knoop indenter under a 10-g load. The electrical resistivity measurements were performed with a Tecrad DMO-350 micro-ohmmeter using a custom made four-point probe,* each electrode being separated by 1.27 mm.

3. Results and Discussion

3.1 *Synthesis of TiB_2 Materials*

The differential thermal analysis performed on mixtures of titanium bronze and amorphous boron was used to determine how the synthesis of TiB_2 proceeds. The thermogram shown in Fig. 2 is more complex than those observed for the synthesis of TiB_2 or TiC in ferrous matrices.[4-6]

Upon heating, the powder mixture is a solid-state homogenization of elements. Copper and $TiCu_4$ are formed according to the Cu-Ti phase diagram.[7] This reaction is marked by the exothermic peak starting at 950 °C. The wide endothermic peak between 1015 and 1050 °C corresponds to the melting of the mixture containing Cu, Ti, and B. The highly exothermic reaction peak present at a temperature just below the melting point of pure copper (1083 °C) is characteristic of a rapid reaction occurring in a liquid phase. On melting, the concentrations of boron and titanium dissolved in copper increase up to a level high enough to initiate the formation of titanium diboride. Thereafter, this reaction takes place and proceeds until completion. The same behavior was observed with other mixtures of titanium bronze and boron.[3] The 10 wt% titanium bronze was chosen because it reacts with boron at a temperature very close to the melting point of pure copper.

3.2 *Microstructure of Cu-TiB_2 Materials*

The microstructure of materials synthesized in an electric resistance furnace is shown in Fig. 3. Note that the TiB_2 crystal sizes are between 1 and 5 μm. Despite maintaining these crystals

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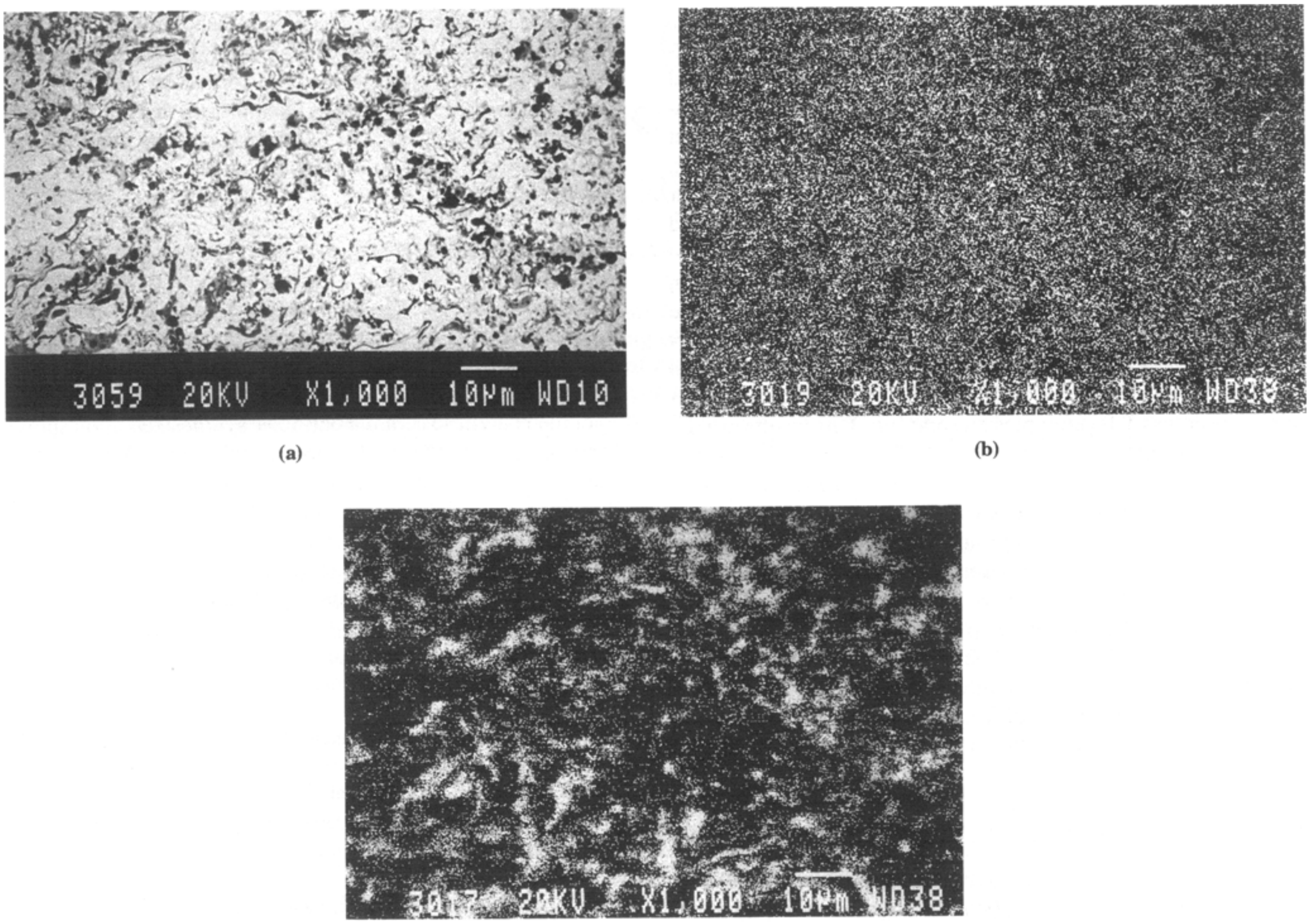
* Products of Ultra Optec Inc., Boucherville, Québec, Canada.



(a)

(b)

(c)

Fig. 4 Scanning electron micrograph of the Cu-TiB_2 coating. (a) Backscattered electron image. (b) Copper elemental image. (c) Titanium elemental image.

for 1 h at 1200 °C, they did not grow to a large extent, indicating the good stability of the material for prolonged high-temperature exposure. The calculated TiB_2 volume content with the copper matrix should reach 24.4 vol%. The volume fraction of TiB_2 present in this composite material determined by analyzing scanning electron microscope images is 26.3 vol%. The measurement was performed on ten frames covering an observed area of 4750 mm^2. However, on the micrograph presented in Fig. 3, the distribution of TiB_2 in the copper matrix is not uniform, with areas highly rich and depleted in TiB_2. Thus, the measured volume fraction greatly depends on the observed area and varies from 12 to almost 50 vol%.

A residual Ti concentration lower than 0.3 wt% in copper was also determined using energy dispersive X-ray spectrometry (EDX). This value was the mean of ten measurements made on areas depleted in TiB_2. However, the actual content of Ti soluble in copper should be lower. Even though no TiB_2 is observed in the analyzed areas, titanium X-rays can be generated within TiB_2 because of electron beam broadening effects. Furthermore, generally X-rays are less absorbed by light atoms like boron than by heavier ones such as copper. A titanium X-ray emitted within a TiB_2 matrix should be less absorbed by TiB_2 than a titanium X-ray generated within a copper matrix. The residual Ti content was determined assuming that only copper and titanium were present in the sample. Some X-rays are probably generated by TiB_2 in the vicinity of the electron probe, and consequently, their absorption in TiB_2 should be lower than in a Cu matrix. Therefore, the amount of titanium in solution in Cu should be overestimated because calculations do not take into account this difference in species absorption. In the binary Cu-Ti phase diagram proposed by Murray,[7] the maximum solubility of titanium in copper is 8 wt% at 885 °C. A concentration of 2 wt% titanium in solution in copper after mechanical alloying of TiB_2 with a copper matrix has been reported.[8] The low concentration of 0.3 wt% found in the current Cu-TiB_2 materials results probably from boron, which drastically limits the solubility of titanium in copper.

3.3 *Microstructure of Plasma Sprayed Cu-TiB_2 Coatings*

The microstructure of a Cu-TiB_2 coating obtained by plasma spraying is shown in Fig. 4. Within this coating, the TiB_2 crystals cannot be discerned, and their size is below 1 µm. The rapid melting of reagents and the rapid solidification of reaction products following the plasma spray process refine the microstructure of Cu-TiB_2 coatings as opposed to Cu-TiB_2 materials molten in a furnace. The darker regions shown in Fig. 4(a) reveal that submicron TiB_2 crystals form clusters within the copper matrix. The Cu and Ti elemental images (Fig. 4b and c) confirm that some regions, darker on the backscattered electron image of Fig. 4(a), are richer in titanium. However, both titanium and copper are present within almost the entire coating, indicating a good distribution of TiB_2 within the copper matrix.

The differences in Ti concentration in the X-ray mapping can be explained by differences in TiB_2 particle concentrations. The nonhomogeneous distribution in TiB_2 could be related to the different phases present in the starting materials (Cu, Ti, Cu_4Ti, and Cu_4Ti_3). Depending on their titanium content, particles can contain more or less TiB_2 after plasma spraying. This results in TiB_2 concentration differences within the coating. For furnace melted materials, a longer heating time favors both diffusion and species homogenization. The TiB_2 volume content within sprayed coatings determined by image analysis is 26 vol%, which is comparable to the volume fraction obtained for Cu-TiB_2 material melted in a furnace.

As opposed to usual plasma sprayed coatings or to those obtained previously by spraying reactive micropellets, it should be pointed out that the microstructure of Cu-TiB_2 coatings is nonlamellar. This microstructural feature, usually related to monolithic materials, indicates that these coatings could exhibit isotropic behavior.

3.4 *Microhardness of Cu-TiB_2 Coatings*

The microhardness of Cu-TiB_2 coatings measured with a Knoop microindentor is 180 (standard deviation of 37 for 6 measurements). In comparison, the furnace melted Cu-TiB_2 material has a hardness of 154 (standard deviation of 50 for 9 measurements). This difference in hardness is the result of the microstructural refinement in sprayed coatings, as mentioned above. The coating hardness is comparable to the hardness of Cu-Co-Be, Cu-Ni-Be, Cu-W, and Cu-Mo alloys and TiB_2-TiC materials obtained by reaction sintering.[9] It is worth noting that pure copper has a maximum hardness of 120 even after severe work hardening.

3.5 *Electrical Resistivity*

The electrical resistivity of Cu-TiB_2 coatings reaches 52 $\mu\Omega \cdot$ cm, which is almost an order of magnitude higher than common copper alloys. It is comparable to the resistivity of steel. There are several reasons explaining this low resistivity. Impurities, and more particularly oxygen which is detrimental to electrical properties, are present within spray powders and are introduced while spraying in air. The formation of TiB_2 clusters within the sprayed coatings likely indicates that the TiB_2 content is high. A large packing of these TiB_2 clusters would certainly modify the electrical resistivity to a large extent.

4. Conclusion

Plasma sprayed Cu-TiB_2 coatings containing fine and dispersed TiB_2 can be obtained by plasma spraying reactive powders constituted of 10 wt% titanium bronze and boron. By this process, up to 25 vol% TiB_2 crystals were introduced into a copper matrix. These ceramic particles, synthesized upon spraying, increases the hardness of copper considerably. After the formation of TiB_2, the amount of residual titanium in the copper matrix remains above the detectability level. The selection of more pure starting materials and their spraying in an inert atmosphere would contribute to increasing the electrical conductivity of these Cu-TiB_2 coatings, making them attractive in electrotribological applications.

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