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Thermal Spraying of Reactive Materials to Form Wear-Resistant Composite Coatings

S. Dallaire

The dispersion of more than 20 vol.% submicrometer ceramic particles within a metallic matrix and the deposition of such a cermet to form a thick and tough coating presents problems. Most of the coating techniques have failed in attempting to homogeneously disperse very fine and hard particles in large amounts while avoiding their decomposition or reaction with the metal matrix during the deposition process. A simple and efficient method has been developed for producing ceramic-containing composite coatings. It consists in synthesizing cermet-based materials and in depositing them by a rapid solidification process such as thermal spraying. Boride- and carbide-based materials have been successfully obtained by plasma spraying reactive powders comprising the basic reagents. These materials, with a microstructure of submicrometer ceramic particles dispersed in a metallic matrix, exhibit good wear-resistant properties (abrasion and sliding wear). Finally, reactive core wire arc spraying is suggested as a flexible way to produce coatings containing up to 25 vol.% TiB_2.

1. Introduction

PROTECTIVE coatings are used to prevent various industrial components from surface degradation by wear. The performance of these coatings is dictated by the composition and microstructure that results from the deposition methods. The ability of the coatings to protect components against aggressive environments involving mechanical attack by eroding or abrading particles is primarily a function of their morphology (form and structure) rather than that of their composition and hardness.

A new approach consisting in dispersing hard and small particles within a metallic matrix is then proposed as a solution to this degradation mechanism. The method is related to the formation of a coating done by the simultaneous synthesis and deposition of cermet-based coatings. Thick coatings containing finely dispersed titanium diboride or titanium carbide crystals are described, and their abrasion or sliding wear resistance is related to their microstructure.

2. Degradation of Materials by Erosion and Abrasion

Ceramic containing materials are mainly selected to ward off severe wear problems such as those met in abrasion and erosion. It should therefore be appropriate to examine these degradation mechanisms to see how microstructure changes could improve materials performance. The erosion mechanisms by which ductile and brittle materials are removed are completely different. Ductile materials fail as a result of impacting particles causing localized plastic flow that exceeds the critical strain to failure in local areas.[1] Erodent particles transported by a liquid or a gas strike the surface and extrude thin microplatelets. The platelets are then further flattened by subsequent particles striking the deformed material. Particles that impact the same localized area bring extruded platelets to their critical strain and rupture portions of them.[2]

The mechanism of erosion of brittle materials (*e.g.*, ceramics) is different. Brittle materials are removed by cracking and chipping mechanisms.[3] The smaller the grain size, then the lower the removal rate. Hard materials are efficient in defeating the impacting particles by either deflecting them at low angles of incidence or causing them to shatter at steep impact angles.[4] In cases where the material consists of both brittle and ductile components, such as tungsten carbide particles bonded in a matrix of cobalt, the composite has the behavior of the volume-dominant material. To defeat the impacting erodent particles, it is generally admitted that the composite should contain at least 80 vol.% of hard phases.[5] Below this value, the impacting particles remain able to plastically deform the ductile binder, folding the hard particles into the binder. High erosion rates are encountered because the composite cannot shatter erodent particles on impact. Higher erosion rates than those with ductile material are often observed because the hard phase restricts the metal binder from plastic deformation. A high stress level is concentrated in the impact area. In abrasion by hard particles, the material is removed by mechanisms similar to those of erosion. These mechanisms involve plastic deformation and extrusion of ductile metal and brittle spalling due to crack propagation within the hard phases.

The degradation mechanisms described above may occur with coatings, depending on whether they have ductile or brittle behavior. There is plastic deformation leading to failure for ductile materials or cracking and chipping for brittle materials. Hard coatings can defeat impacting particles as long as they remain bonded to the substrate. However, as most of the coatings have a microstructure different from bulk materials, they could behave differently. Physical vapor deposited coatings with a columnar microstructure wear differently from those having equiaxed grains. Plasma-sprayed multilayer coatings composed of a stack of alternated soft and hard layers can limit crack propagation. Fine-grained multiphase coatings composed of hard materials

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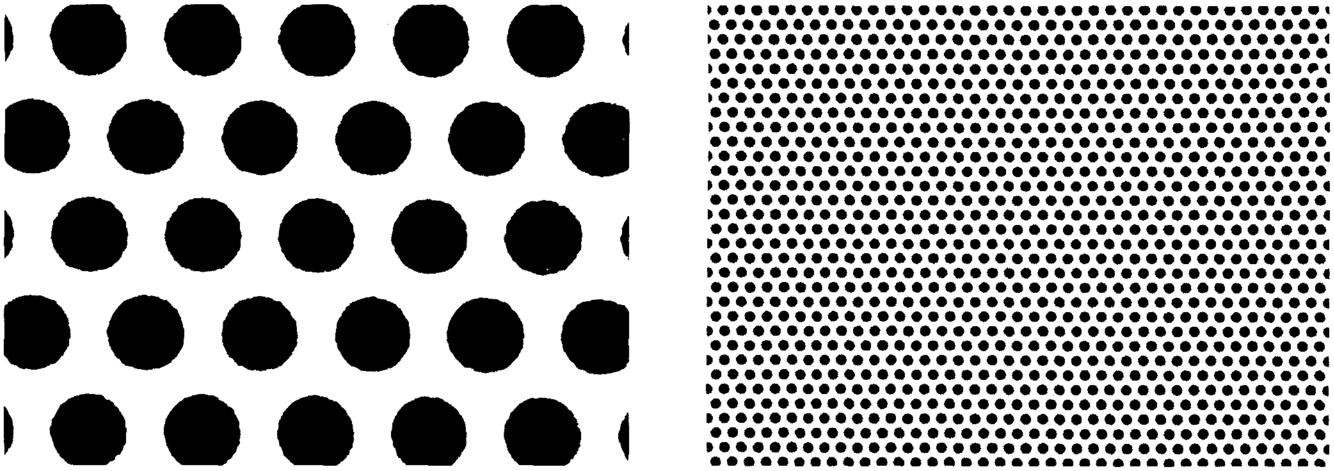
S. Dallaire, Industrial Material Institute, National Research Council Canada, 75 De Mortagne Blvd., Boucherville, Quebec, Canada, J4B 6Y4.



(a) (b)

Figure 1 Schematic of a composite material containing 40 vol.% spherical ceramic particles. The ceramic particle size and the distance between ceramic particles in (b) are ten times less than in (a).

dispersed in a metal matrix would be tougher and more resistant to crack propagation than pure ceramic coatings while ensuring wear resistance.

3. Material and Coating Concept Development

It has been considered that a composite material (cermet-type) consisting of hard particles bonded in a ductile matrix could form a coating that defeats impacting particles provided it is dense and contains a large amount of hard phases. A skeleton of touching hard particles leaving little space for the metal binder is thought to be efficient if its volume content is as high as 80%.[5]

Rather than considering only the volume content of hard particles, it may be more appropriate to take into account the size of hard particles and their dispersion within the metal or the distance between them. For the sake of simplicity, both materials described schematically in Fig. 1 contain 40 vol.% hard particles. However, the distance between particles and the size of these particles are completely different in both materials. To decrease the area exposed to impacting particles, the distance between hard particles for the material shown in Fig. 1(a) should be decreased. In practice, this could only be done by increasing the volume content. By comparison, the material shown in Fig. 1(b) could contain a lesser volume content of hard particles without increasing significantly the distance (mean free path) between these particles, provided it is smaller than the size of impacting particles.

A composite material containing small hard particles homogeneously dispersed within a ductile matrix would resist abrasion and erosion better than the cermet containing large particles separated by a distance large enough for the intrudent particles to come in contact with the ductile metal. A composite material containing a lesser volume content of small hard particles could be as resistant as a material whose volume content is 80%.

4. Coating Principle

The dispersion of hard phases within a metallic matrix and the deposition of such a cermet to form a thick and tough coating are difficult problems to solve. Introducing and dispersing more than 20 vol.% submicrometer ceramic particles in a metal matrix is technically difficult. Moreover, is there a coating technique capable of producing this type of coating? The plasma spraying technique has been successful in depositing cermet-type coatings. However, the techniques have not been successful in producing a homogeneously dispersed structure of very fine and hard particles in large amounts while avoiding their decomposition during the deposition process.

A different approach has been developed for producing wear-resistant coatings. It consists in synthesizing cermet-based materials followed by their deposition by thermal spraying. The so-called plasma spray synthesis process was first developed for producing TiB_2-metal coatings,[6,7] but it is not limited to this type of coating.

5. Coatings Containing TiB_2

5.1 *Synthesis of* TiB_2

The better way to ensure a good dispersion of fine TiB_2 crystals into a metal matrix and a perfect bonding between the metal and the boride consists in synthesizing TiB_2-metal materials through the reaction of a titanium-bearing alloy with boron or boron compounds.[8-10] This titanium-bearing alloy can contain different elements such as iron, aluminum, nickel, molybdenum,

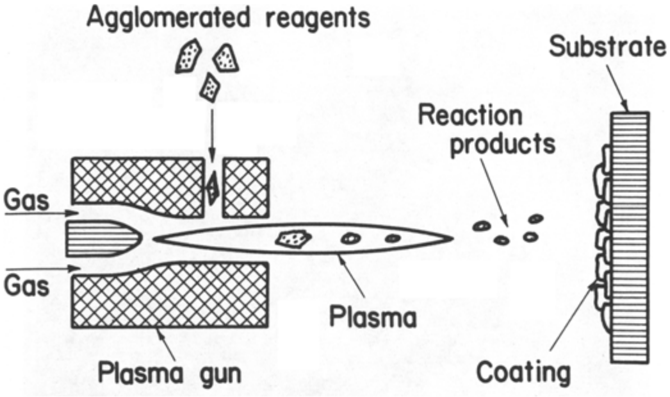


Figure 2 Schematic of the plasma spraying of reactive powders.

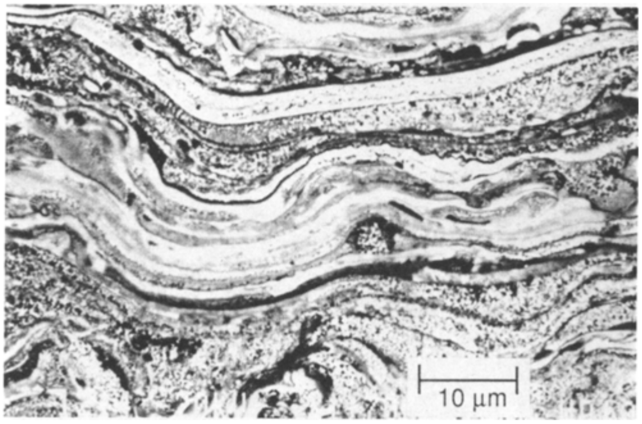


Figure 3 Microstructure of a plasma spray synthesized TiB_2-Ni-Fe coating. Dark thin lamellae are titanium boride-rich or oxide stringers. Lighter lamellae are richer in nickel, whereas gray ones consist of iron and TiB_2.

cobalt, copper, or mixtures of these. For the sake of simplicity, the description of the process is limited to TiB_2-Fe cermets.

Cermet coatings based on TiB_2 can be produced in two different ways. The first one consists in synthesizing TiB_2 through the reaction of a ferrotitanium alloy with elemental boron and in depositing the reacted products onto a substrate by plasma spraying.[8] When the chemical composition is adjusted so that the [B]/[Ti] atomic ratio is 2.0, the exothermic reaction that occurs between reactants can be represented by the following equation:

$$FeTi + Ti + 4\,B \rightarrow 2\,TiB_2 + Fe \qquad [1]$$

Another means that could be less expensive was also developed. This different route uses the principle of the auxiliary metal bath process to synthesize TiB_2. The auxiliary metal bath process, known also as the Menstruum process, consists in promoting the reaction between elements by dissolving them in a liquid metal. TiB_2 crystals can be synthesized in an iron auxiliary bath by melting a ferrotitanium and ferroboron mixture.[11] When the constituents form a mixture in which the [B]/[Ti] atomic ratio is 2.0, the reaction that occurs can be represented by the following equation:

$$FeTi + Ti + 4\,FeB \rightarrow 2\,TiB_2 + 5\,Fe \qquad [2]$$

The synthesized products depend on the reaction temperature as well as on the [B]/[Ti] atomic ratio. When this ratio is less than 2, the reaction products contain Fe and FeTi compounds.

Similarly, Fe and TiB_2 compounds are found in the products when this ratio is greater than 2. The temperature necessary to initiate the exothermic reaction is 675 °C[8] and the temperature to complete the endothermic reaction is above 1700 °C.[9,10] Temperatures within a plasma greatly exceed the reaction temperatures. However, because these temperatures are not uniform in a plasma jet, it is expected that particles will follow trajectories allowing them to reach the appropriate temperatures for completion of the reaction. After injecting reactive powder micropellets comprising the reagents (ferrotitanium + boron or ferrotitanium + ferroboron) into the plasma, the reaction takes place and TiB_2 is synthesized. Whatever the route chosen (Reaction 1 or 2), X-ray diffraction analysis confirmed that the main reaction products are TiB_2 and iron. After the synthesis, as shown in Fig. 2, the reaction products are propelled by the plasma onto a substrate resulting in the deposition of a cermet coating containing TiB_2.

5.2 *Micropellet Fabrication and Coating Deposition*

Details related to the composition, fabrication, and characterization of reactive powders as well as their deposition by plasma spraying and the characterization of coatings obtained have been described previously.[8-10] In short, the reactive powders were prepared by using an agglomeration technique (mechanical or spray drying). These powders, sorted in adequate size fractions, were sprayed with conventional plasma spray equipment under ambient atmosphere. X-ray diffraction analysis was used to characterize the reaction products and coatings. Metallographic examination was done with optical and scanning electron microscopy. Finally, the wear resistance of diamond-ground coatings was measured in accordance with the standardized low stress ASTM G-65 method.

5.3 *TiB_2-Fe Coating Microstructure and Performance*

After leaving the plasma gun, the melted droplets containing the reaction products are propelled by the high-velocity gas against a clean surface, as shown in Fig. 2. A coating consisting of overlapping lamellae is progressively formed. Upon impinging the substrate, the surface droplets undergo rapid solidification which further enhances the microstructure of the coating as opposed to droplets of the same composition solidified in a furnace. Figure 3 shows the microstructure of TiB_2-Ni-Fe coatings obtained by the exothermic route, and Fig. 4 shows the uniformity of the dispersed TiB_2 crystals. Even if these crystals were synthesized from impure starting materials, it was found that the solubility of impurities in TiB_2 is low[11,12] and that oxygen was picked up by boron to form B_2O_3, which is thought to be vaporized during spraying.

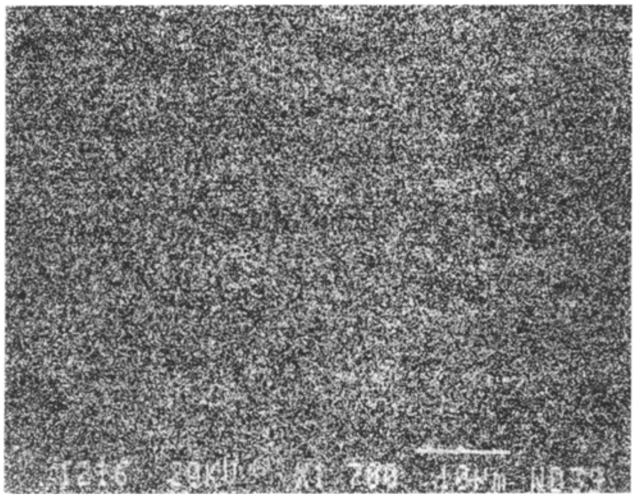


Figure 4 Scanning electron micrograph for titanium within the TiB_2-Fe-Ni coating.

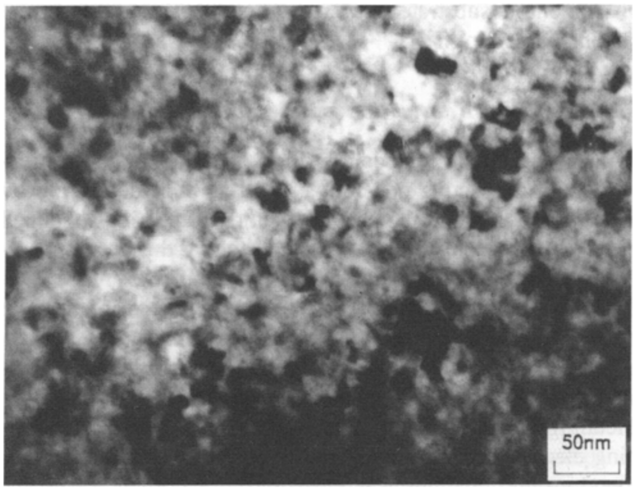


Figure 6 Transmission electron micrograph of a TiB_2-Fe coating showing fine grains (10 to 60 nm) of iron, TiB_2, and FeTi.

The resultant 1-mm thick TiB_2-metal coatings possess moderate microhardness: 15.2 and 13.73 GPa (load, 1 N) for the coatings plasma spray synthesized via the exothermic and endothermic routes, respectively. Even if these cermet coatings contain little porosity, they have been submitted to the dry sand/rubber abrasion test. The performance of TiB_2-Ni-Fe coatings containing 60 vol.% TiB_2 was found comparable to that of high-energy WC-Co coatings that contain 82 vol.% WC. The volume loss is about 15 mm^3, whereas it reaches 300 mm^3 for bulk steel. Because the degradation of plasma-sprayed coatings varies directly with the level of defects and porosity, the performance of these coatings can be improved by decreasing the porosity between individual splats.

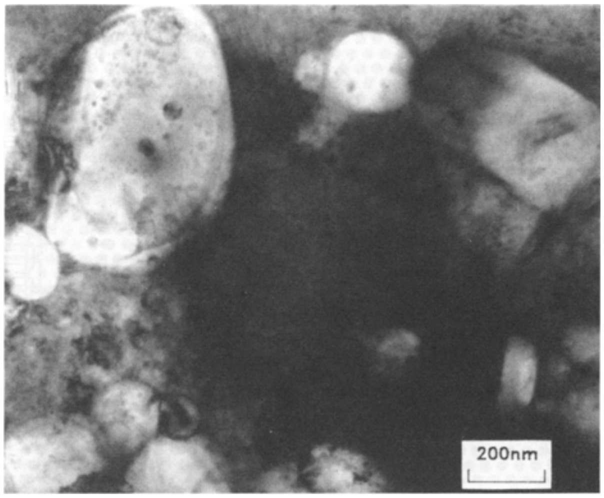


Figure 5 Transmission electron micrograph of a TiB_2-Fe coating showing TiB_2 particles ranging from 350 to 700 nm in a matrix of α-Fe and fine TiB_2 particles (50 to 200 nm).

Analytical transmission electron microscopy characterization was undertaken to elucidate the fine microstructure of these TiB_2-Fe coatings.[13] Energy dispersive spectroscopy (EDS) using an ultra-thin window (UTW) detector and electron energy loss spectroscopy (EELS) techniques allowing the detection of light elements were used. These analyses showed that these TiB_2-Fe coatings contain TiB_2 particles ranging from 10 to 700 nm in size (Fig. 5 and 6) dispersed in a matrix containing mainly iron and some residual FeTi.

The uniform dispersion of very fine and hard particles less than 1.0 μm in size in a ductile iron-based matrix seems to be responsible for the good wear resistance observed during testing. Indeed, the hardness of these TiB_2-metal coatings is not very high (less than 15.2 GPa), and the volume of hard phases is less than 60%.

6. Coatings Containing TiC

Carbide-based materials have also been investigated extensively.[14] Because the stoichiometry of carbides is of concern while considering their mechanical and chemical properties, carbide-based materials were more difficult to deposit in thick and dense coatings.[14] Without describing this synthesis in detail, it is worth mentioning that the carbide synthesis and deposition process is as simple as the boride deposition process. For instance, when spraying reactive powders comprising ferrotitanium and graphite, the following reaction

$$FeTi + Ti + C \rightarrow 2\,TiC + Fe \qquad [3]$$

occurs and TiC-Fe coatings are obtained.[15] The microstructure of these coatings consisted of alternate TiC-rich and TiC-poor lamellae (Fig. 7) of different hardness. These layers can be modified by changing the composition of reactive powders and their spraying conditions.[16] The coatings containing fine and

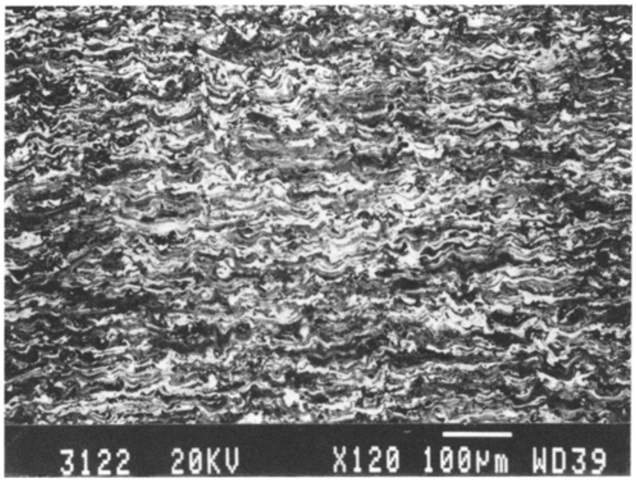


Figure 7 Microstructure of a plasma spray synthesized TiC-Fe coating containing 40 vol.% TiC.

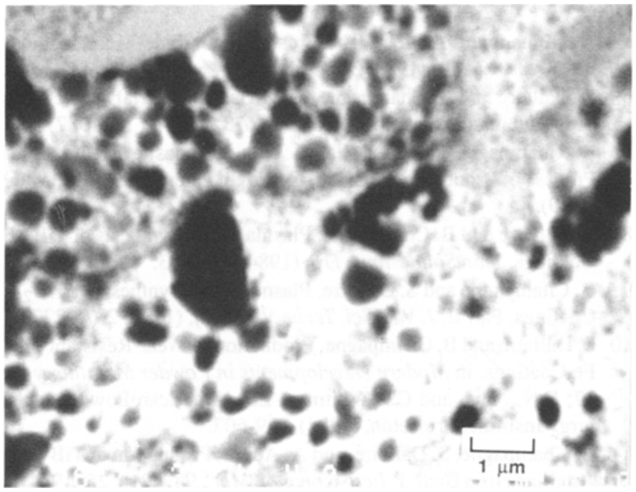


Figure 8 Scanning electron micrograph of a TiC-rich lamella within a 60 vol.% TiC showing the size and shape of TiC crystals (black spots).

rounded TiC crystals (Fig. 8) possess alternate TiC-rich and TiC-poor layers whose hardness varies according to fabrication parameters. This hardness lies between 9.81 and 17.65 GPa for TiC-rich layers and between 2.94 and 5.88 GPa for TiC-poor layers.

The sliding wear resistance of TiC-Fe coatings containing 60 vol.% TiC against steel, as measured in accordance with the test procedure recommended by the Versailles Advanced Materials and Standards (VAMAS) program,[17] is high when sintered reactive powders are sprayed. The scar depth reaches nearly 2 µm after a sliding distance of 1 km, being three times less deep than that of coatings obtained by thermal spraying spray-dried TiC-Fe composite powders. Under the same conditions of testing, a steel ball sliding over a steel surface forms a scar of 90-µm depth.[18]

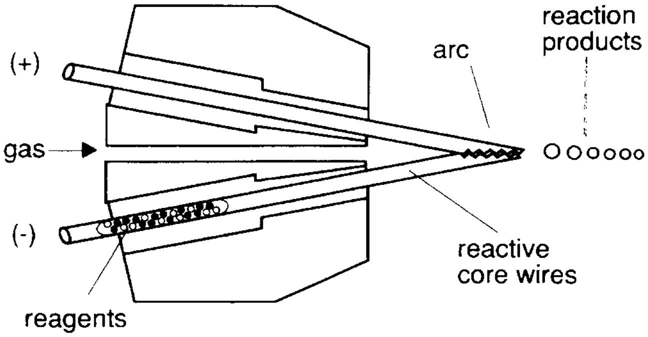


Figure 9 Schematic of the arc spraying of reactive core wires.

The microstructure of these multiphase and multilayer TiC-coatings seems to be responsible for their good behavior. The inevitable and minute debris generated during the sliding is trapped within the surface pores and forms a self-lubricating film. This film maintains a low coefficient of friction, before the surface breaks down due to porosity.[18] Although presenting some good wear characteristics, plasma-sprayed coatings using mixtures of metal and carbide powders,[19] agglomerated metal and carbide powders,[20, 21] or metal-coated carbide powders[22, 23] do not have the same behavior because most of them contain angular particles with sizes larger than the lamella thickness. Conversely, a multiphase hard lamella lying on a ductile one does not behave as a plowing element in the same fashion as a large and angular carbide particle.

7. TiB_2-Containing Materials by Reactive Core Wire Arc Spraying

Another approach was performed to facilitate the deposition of the materials, to lower their cost, and to increase the deposition rate. It consists of depositing TiB_2-containing materials by using the flexible arc spraying technology. The arc spraying technology, widely used in industry, offering considerable advantages and requiring only 10% of the energy involved in plasma spraying, has not been improved since it was invented by Schoop in 1915.[24] Because it requires conductive wire, arc spraying has been limited to the deposition of metals.

Coatings containing TiB_2 were synthesized by arc spraying reactive core wires containing basically the same reagents as those used in reactive powders (FeTi and B). These reactive core wires consist of metal sheaths that wrap around densified cores of the reagents. Arc spraying with a conventional gun (Fig. 9), but using argon as an atomizing gas to avoid oxidation of reagents, results in few millimeter thick coatings of coarser microstructure than coatings obtained by plasma spraying reactive powders (Fig. 10). The coating microstructure depends on the core wire fabrication, as well as the wire deposition parameters that affect the reaction temperature.[25] Even though these coatings do not exhibit the same coating integrity as those obtained by plasma spraying reactive powders, they contain up to 26 vol.% TiB_2[25] and some hard-phase features (such as those shown in Fig. 11) that could be useful for specific wear applications.

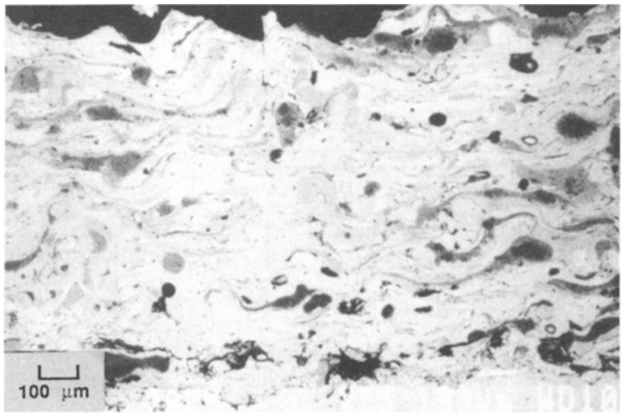


Figure 10 Scanning electron micrograph of a stainless steel coating containing 26 vol.% TiB_2.

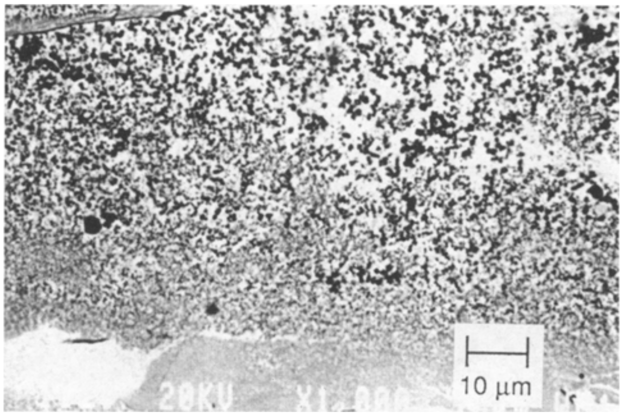


Figure 11 Scanning electron micrograph of a large arc-sprayed lamella containing finely dispersed TiB_2 crystals.

8. Conclusion

The spray synthesis process that involves the plasma spraying of reactive powders or arc spraying reactive core wire is aimed at the synthesis and deposition of coatings containing hard ceramic phases without the necessity to reach the melting point of these ceramics. It was found to refine the grain size below the micrometer level and to disperse the synthesized ceramic within a ductile matrix. As it generates materials with properties that have not been expected based on previous studies (*e.g.*, wear-resistant materials), the spray synthesis process is powerful and can be considered unique in the area of materials technologies.

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