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Reactive Plasma Spraying of Wear-Resistant Coatings

R.W. Smith and Z.Z. Mutasim

A method for producing wear-resistant, carbide-reinforced coatings has been investigated. A conventional low-pressure plasma gun has been modified with a downstream reactor into which carbon-containing gases are mixed, heated, and disassociated. The disassociated gas ions—H* and C* —are subsequently brought into contact with heated, molten metal matrix powders. Experiments with NiCr/Ti blends and W powders have shown that uniformly dispersed carbides such as, TiC, Cr_xC_y, WC, and W_2C were formed *in situ* on the metal precursor powders during deposition. The *in situ* formed particles, being formed directly from the matrices, show excellent matrix cohesion and lead to high and uniform deposit microhardnesses. The process is described and several evaluations of materials, reactive gases, and spray conditions are reported. Microanalysis of the coatings are presented, microhardness values are reported, and XRD identifies the *in situ* formed phases.

1. Introduction

WEAR-RESISTANT coatings are widely used in aerospace and other industries to increase the life of moving components and/or to improve the performance in severe environments. Thermally sprayed metal matrix coatings reinforced with hard carbide particles are well-established materials for many of these applications.[1-3] Wear resistance is improved when carbide particles are embedded in a tough, metallic matrix where the carbides act as bearings for the sliding surfaces, reducing friction coefficients, preventing adhesive metal transfer, or in resisting the metal removal from erosive particles.[4] These coatings are typically composites consisting of a soft binder matrix, Co or NiCr, reinforced with hard WC or Cr_2C_3 particles that are from 1 to 15 μm in size. Powders that incorporate WC, Cr_xC_y, and more recently TiC particles[5] have been developed and are being thermally sprayed with plasma or HVOF processes for producing wear-resistant coatings.[6-8] These investigations have shown that uniform secondary carbide phase distributions consistently produce the most reliable wear-resistant coatings.

These composite coatings are formed from thermally spraying particles that have been produced by (1) mixing blends of carbides and metals, (2) cast and crushed mixtures, or (3) by agglomerating the metal and carbide particles followed by either spray drying, sintering, or possibly plasma densification.[9] Previous work has reported the effects of powder manufacturing on the structure and wear properties of sprayed coatings.[10] It has been observed that wear rates vary with carbide distribution, volume percent, and morphology. Therefore, powder production methods, which affect all these properties, contribute significantly to the wear resistance of thermal spray coatings. Engineered powders that control these powder features are now available and have significantly improved the wear performance. However, many of these engineered powder production methods increase the cost of powders over the constituent raw materials by a factor of four or more, thus making some engineered powder production less economical. In addition, the cohesion between the carbide phases and the matrix may be relatively weak, allowing the particles to fragment during thermal spray processing. Powder particles may fragment during handling, feeding, in flight because of high particle thermal stresses,[11] or on impact against the substrate.

Reactive plasma spraying is an alternative process that promises to eliminate many intermediate powder manufacturing steps while producing improved wear resistance through the incorporation of fine and uniformly dispersed carbide phases. These carbide phases, being formed *in situ* directly from the metal matrices, should have stronger cohesion with the matrix and should result in improved wear resistance. Reactive plasma spray coating processing and its use in forming wear coatings is described in this article, centering on recent investigations with NiCr/TiC and W/WC coatings.

Plasma synthesis has been used for the production of ultrafine (> 1 μm) powder particles from gaseous precursors.[12-14] These investigations confirmed the utility of thermal plasma synthesis for forming carbides, borides, and oxides from gaseous and/or solid precursors. Reactive plasma spray coating extends these results into the spray forming of composites, using the reactive capability of the plasma environment in combination with the plasma spraying of metal particles. In the process,

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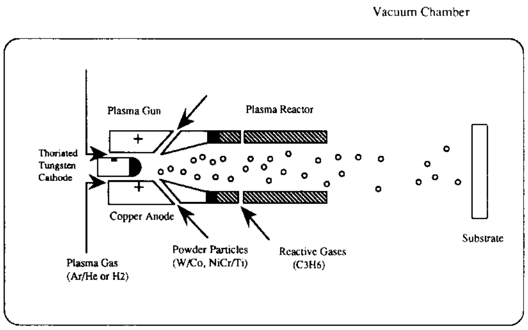

Figure 1 Schematic of plasma reactor/plasma spray system.

the reactive ionic species, generated from disassociating reactive gas precursors, react with heated metal powders forming carbides and/or other products on the heated or molten metal particle surfaces. Product films of varying thicknesses form, depending on the particle sizes. The reacted carbide films and/or other products are then carried to the deposit where the film fractures and becomes dispersed into the unreacted metal matrix, as shown in Fig. 1. This composite materials synthesis process is being investigated for its application in producing wear-resistant coatings.

In this investigation, propylene gas has been injected into the plasma zone via a reactor (Fig. 1), making use of incomplete but plasma-enhanced reactions to produce reacted WC and TiC films on tungsten (W) or titanium (Ti) particle surfaces, respectively, as they travel and contact the carbon species in flight. The investigators have used the low-pressure plasma spray process to form a broad range of materials, coatings, and thicker structural materials, with carbide, oxide, nitride, and silicide. These dispersoids have been used as strengthening phases in materials forming high-temperature, stable, and more coherent phases that have been formed from the matrix, thus providing higher matrix binding forces that make these composite materials more resistant to deformation.

2. Processing

2.1 *Objective*

Typically, when sprayed in ambient atmospheric conditions, deposits have uncontrolled levels of oxides and nitrides due to interaction of the molten particles with the atmosphere that is entrained in the plasma in the plasma jet. Therefore, plasma deposition in controlled, inert atmospheres, and at low pressures has been introduced to improve the deposit quality by lowering the potential for uncontroled deposit inclusions. Reactive plasma spraying uses the environmental control of the low-pressure plasma spray process[14] and reintroduces, in a controlled way, "Contaminants" to produce reinforced composites with microstructures engineered for optimum performance. The objective of this investigation was to design a reactive plasma spray process for producing wear-resistant Ti-C and/or WC-reinforced metal matrix coatings, thus offering an alternative method for producing wear resistant coatings from less expensive blends of metal powders.

2.2 *Process Description*

Figure 2 illustrates the plasma process in combination with an "environmental" chamber that controls the inert background gas from 1 torr to atmospheric pressure. A conventional dc Electro-Plasma Inc. (EPI 03CA) plasma gun was modified by attaching a plasma reactor downstream from the plasma torch, as illustrated by Fig. 1. This concept extends the reaction zone, increases the available reaction times, increases the precursor gas mixing, and minimizes any undesirable interactions between the torch electrodes and the reactive gas precursors. Electrode interaction, such as the formation of WC on the cathode or oxidation of the copper anode wall at the arc foot, are prevented because the reactive gases are injected downstream from the arc. The design of the plasma gun and the power supply low open circuit voltages prevent an extended arc, thus keeping the arc inside the plasma gun and out of the reacting regions. The pilot plasma jet, produced in the plasma gun, provides the main particle heating, accelerates the injected powder particles into the downstream "plasma reactor," and disassociates the injected reactive gases. The plasma reactor mixes the reactive gases with the plasma jet, maintains effective heating and melting of powder particles in the reaction zone, and separates the reactant gases from the plasma gun electrodes.

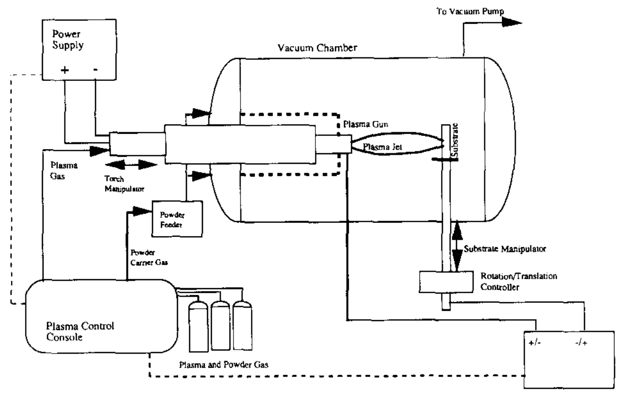

Figure 2 Schematic of low-pressure reactive plasma spray equipment.

A blend of the metal powder, containing the carbide-forming metals (*i.e.*, W, Ti, Cr, etc.) and the binder metal is injected into the plasma gun portion of the reactor. The concept is to introduce the reactants that produce WC, TiC, and Cr_xC_y into the reactor while ensuring a sufficient supply of metal binder phase that remains molten on impact of the particles. Plasma gun parameters and nozzle design (copper anode in Fig. 1) are selected to yield well-melted, centrally located powder distributions that are subsequently injected into the plasma reactor region. Reactive gases such as methane, propane, propylene, acetylene, or combinations thereof then form the desired carbides. The C-to-H ratio and binding energies must be considered in optimizing the performance of the reactor and for the structure and composition of the coating.

2.3 *Experimental Procedure*

Two different types of plasma-sprayed coatings were produced from mechanically blended Ni-20wt.% Cr and 40 vol.% Ti and from pure tungsten powders. These materials were used as feedstock to subsequently synthesize NiCr/TiC- and WC-reinforced wear coatings. Tungsten was selected to test the reactor performance with higher melting range materials and to assess its ability to form WC when deposited with methane (CH_4) and propylene (C_3H_6). TiC and Cr_xC_y were to be produced in a NiCr matrix, and WC was to be produced in a tungsten matrix. The respective increase of deposit hardness values and the formation of W-WC or TiC in NiCr composite coatings were expected to yield improved wear resistance. The goal of the investigation was to evluate the possibility of forming (1) NiCr/ + TiC/Cr_xC_y and (2) WC/W coatings directly from metal powder blends.

The powder blends, –44 μm (–325 mesh) in size, were injected into an Electro-Plasma, EPI-93 plasma gun through two ports radially located, but tangentially inclined, inside the nozzle throat (9 mm in diameter) at 12° upstream angles. An EPI volumetric feeder was used at 100 g/min. The plasma gun was operated with Ar/He and/or H_2 gas mixtures, and the plasma arc current was fixed at 1100 A with voltages ranging between 38 V for Ar/He and 50 V for Ar/H_2 plasma gas mixtures. The pressure inside the spraying chamber was kept constant at 200 ± 10 torr. The deposit substrates, 2.5- by 7.5- by 0.3-cm steel coupons, were translated at 7.5 cm/sec, and all deposits, including the baseline coatings, were deposited at a distance of 12.5 cm from the end of the reactor. The substrates were grit blasted with 60-mesh alumina and ultrasonically cleaned in solvent prior to spraying. Deposition times were 1 min, aiming for coating thicknesses of 0.3 to 0.5 mm.

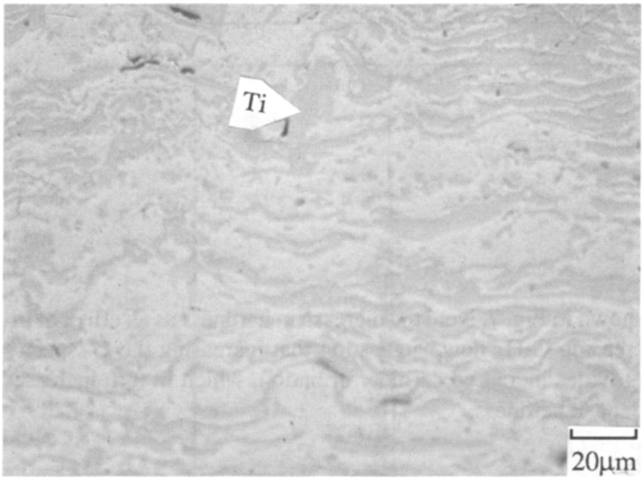

Figure 3 Optical micrograph of plasma-sprayed Ni-Cr/Ti deposit sprayed with 8 slm Ar in reactor.

Initially, Ni20wt.%Cr + 40 vol.% Ti and the W powders were deposited through the plasma without any reactive gases to establish coating baseline structures that could be compared to deposit structures made with the reactive gases. The powders were then deposited with C_3H_6 (propylene) to evaluate the production of Cr, Ti, or W carbides. Methane and propylene reactive gas flow rates were varied from 4 slm to 8 slm to assess the effect of the carbon gases on the coating structures and compositions, as well as to assess the reactor performance. Reacted and unreacted Ni20wt.%Cr + 40 vol.% Ti and W composite deposits were metallographically evaluated to determine the extent of reactions between the powder particles and gas precursors, and the subsequent dispersions of second phase products in the Ni-Cr-Ti and W matrices. Deposit structures were studied as a function of reactant gas type and flow rates. Deposit hardness values were evaluated (Vickers hardness) to determine effects of second phase dispersion in the Ti and W material systems. X-ray diffraction analysis on collected powders and deposits was carried out to identify phases produced during the process.

3. Results

3.1 *Ni20wt.%Cr + 40 vol.% Ti*

Figures 3 and 4 are optical micrographs of Ni-Cr-Ti deposits sprayed with Ar and C_3H_6, respectively. Figure 3 shows Ti-rich regions as dark phases that are uniformly distributed in a white-appearing NiCr matrix. The Ti splats are lenticular in shape and well distributed, ranging from 2 to 5 μm thick and 10 to 50 μm long. In Fig. 4, the C_3H_6 reactively sprayed deposit microstructures exhibit an entirely different structure from that of Fig. 3. Note the absence of any clear distinction between the Ti and NiCr phases and the presence of very fine particulates. The optical photomicrograph resolution prevents a clear distinction from being made; however, the particulate relief shown in Fig. 4 does indicate the presence of fine (<1 μm) carbide particles. To better demonstrate the formation of TiC in metal matrices, see Fig. 5,

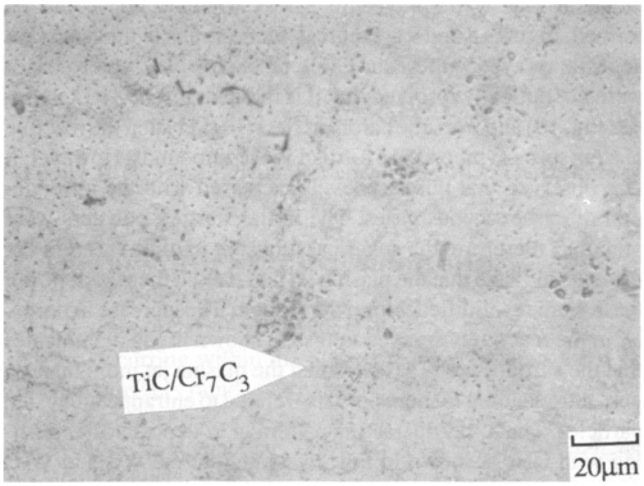

Figure 4 Optical micrograph of reactively sprayed Ni-Cr-Ti deposit sprayed with 8 slm C_3H_6.

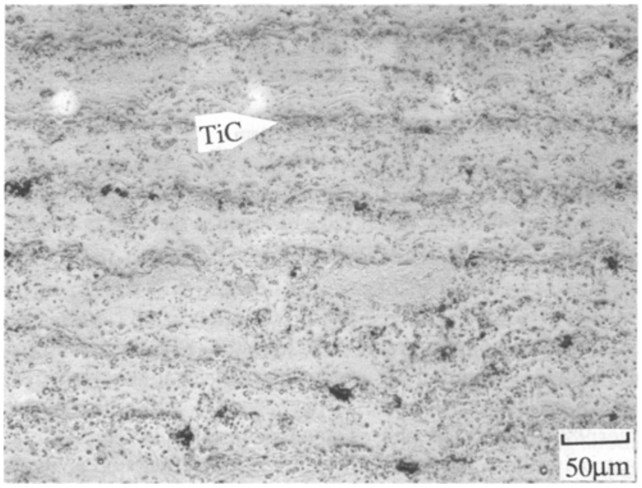

Figure 5 Photomicrograph of reactively deposited Ti with 8 slm propylene.

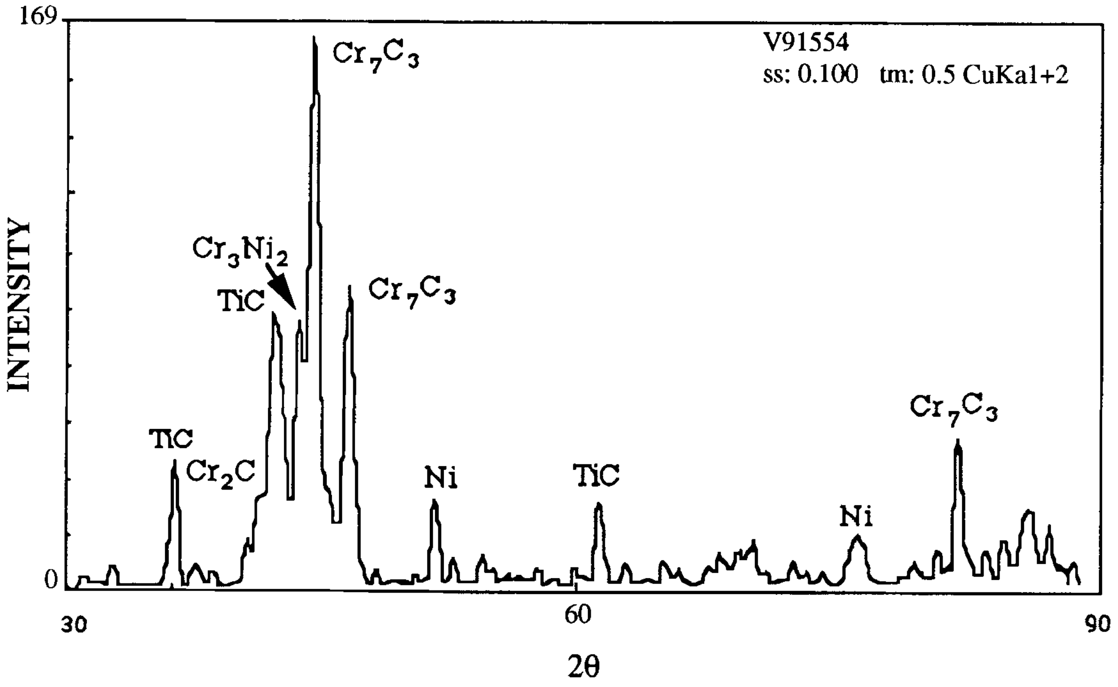

Figure 6 X-ray diffraction pattern of Ni-Cr-Ti deposit sprayed with 8 slm C_3H_6.

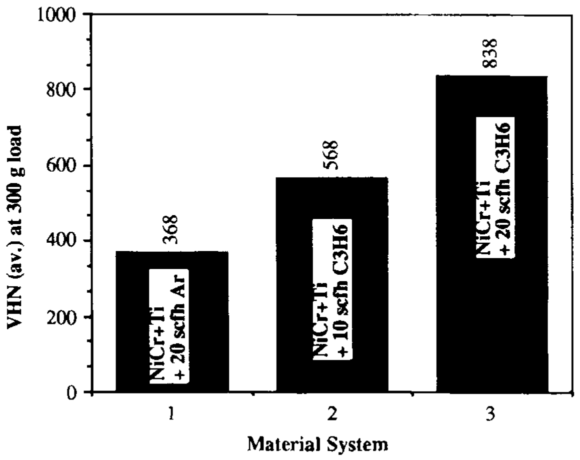

Figure 7 Room temperature microhardnesses of Ni-Cr-Ti deposits: System 1 is Ni-Cr-Ti sprayed with argon as reactor gas, while Systems 2 and 3 were reactively sprayed with C_3H_6.

which is a photomicrograph of Ti deposited with propylene gas showing the formation of carbides (dark phase in relief) distributed in the Ti (white-appearing background). All coatings were over 98% dense. The phases standing in relief to the Ni-Cr-Ti matrix in Fig. 4 were determined by X-ray diffraction analysis (XRD) (Fig. 6) to be Cr_7C_3, Cr_2C and TiC.

Room-temperature microhardnesses (average values of ten indentations) of unreacted and reacted Ni-Cr-Ti deposits are shown in Fig. 7. Note the increase in hardness as an effect of increasing C_3H_6 flow, suggesting that increasing the C^* species provides increased carbide formation, which in turn increases deposit hardness.

3.2 *Tungsten*

Tungsten, a high-temperature (3422 °C melting point) and high-density (19.3 g/cm^3) refractory metal, was selected to evaluate the performance of the reactor in this temperature range. It was also sprayed to assess whether WC could be formed. Figures 8 and 9 are optical micrographs of tungsten (W) deposits sprayed with Ar and C_3H_6, respectively. Carbide phases were not optically resolved, but it is indicated from XRD analysis (Fig. 10) and from the hardness data (Fig. 11) that the reactive plasma spray synthesis has formed WC compounds. However, it was observed that porosity levels increased with the introduction of carbonaceous gases. The initial starting powders were granular; therefore, the spherical tungsten particles seen in the deposits indicate that the plasma jet had melted the powders, but these were resolidified within the reactor. The increase in porosity in the reactively sprayed tungsten, shown in Fig. 9, indicates that the carbonaceous gases cooled the plasma jet more than argon, thus, leading to more porosity related to entrapped tungsten particles. The X-ray diffraction pattern of W deposits after reacting with CH_4 is shown in Fig. 10. Note that the WC and W_2C peaks indicate that plasma-synthesized tungsten compounds were formed. The WO_2 is believed to be carried into the deposit from the feedstock powder surfaces.

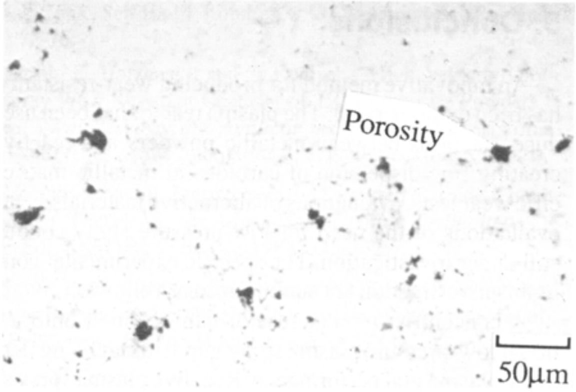

Figure 8 Optical micrograph of W deposit sprayed with 8 slm Ar.

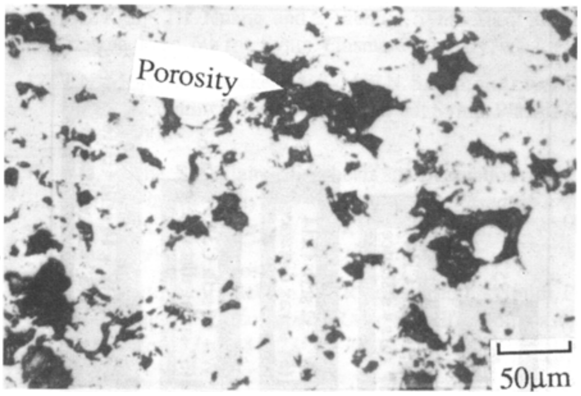

Figure 9 Optical micrograph of W deposit sprayed with 8 slm C_3H_6.

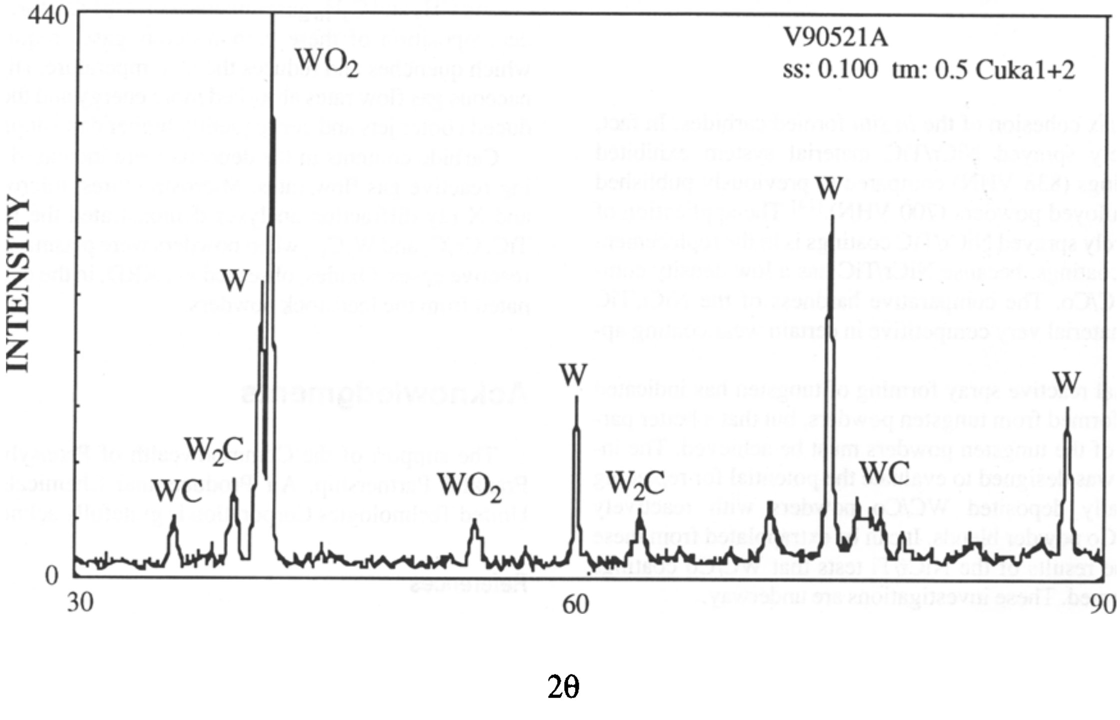

Figure 10 X-ray diffraction pattern of W powders collected after spraying with 8 slm C_3H_6.

4. Discussion and Applications

It is difficult to fully understand the exact reaction processes that are occurring within the plasma reactor, because the reaction rates are very rapid, approximately 10 to 50 msec. However, the nature of the reactions can be postulated, and there is information concerning the reactions from XRD results that indicate the final products.

Ni20wt.%Cr + 40 vol.% Ti is the lower melting point material system of the two evaluated, but has a high heat of TiC formation ($\Delta G_f \approx -200$ kJ/mole). The exothermic reaction of NiCr and Ti with carbon is believed to lead to a high degree of reaction in the plasma environment, resulting in the high degree of Ti and Cr carbide conversion. The fine dispersions of carbides were not easily resolved optically, because the optical resolution is below 1 µm, thus indicating that fine carbides (<1 µm) were formed. Based on the significant increase of the Ni-Cr-Ti composite coatings microhardness, reactive plasma spray forming should produce NiCr/TiC coatings with increased sliding and impact wear resistance. Therefore, reactively spray-formed TiC-reinforced coatings should produce improved wear resistance to plasma-sprayed prealloyed NiCr/TiC powders due to the better

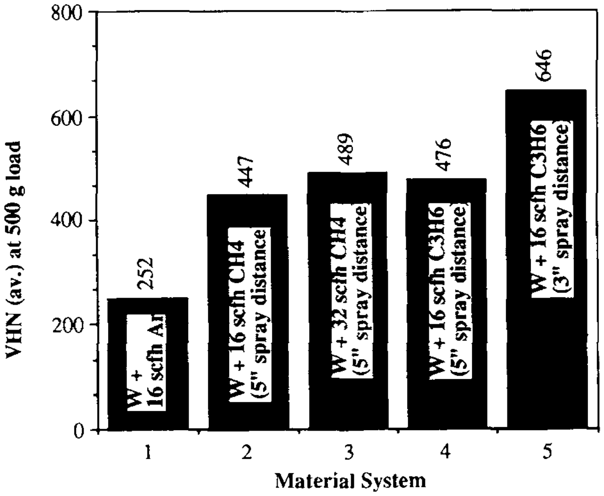

Figure 11 Room-temperature microhardnesses of Ni-Cr-Ti deposits. System 1 is tungsten sprayed with argon as reactor gas, whereas Systems 2 through 5 were reactively sprayed with CH_4 or C_3H_6.

carbide/matrix cohesion of the *in situ* formed carbides. In fact, the reactively sprayed NiCr/TiC material system exhibited harder coatings (838 VHN) compared to previously published data of prealloyed powders (700 VHN).[14] The application of such reactively sprayed NiCr/TiC coatings is in the replacement of WC/Co coatings, because NiCr/TiC has a low density compared to WC/Co. The comparative hardness of the NiCr/TiC make this material very competitive in certain wear coating applications.

The initial reactive spray forming of tungsten has indicated that WC is formed from tungsten powders, but that a better particle sizing of the tungsten powders must be achieved. The investigation was designed to evaluate the potential for replacing conventionally deposited WC/Co powders with reactively sprayed W/Co powder blends. It can be extrapolated from these tests and the results of the NiCr/Ti tests that WC/Co coatings could be formed. These investigations are underway.

Tungsten has a higher melting point and lower carbide heat of formation ($\Delta G_f = -37$ kJ/mole), than TiC, however, WC and W_2C formation did occur. The microhardness increase in the deposited W powders, after reacting with CH_4 and C_3H_6, suggest that very small carbides can be formed. WC formation was not visible in optical microscopy, but XRD showed WC and W_2C peaks, indicating that a plasma-formed W/WC composite was produced. Thus, it can be concluded that a combination blend of W with Co powders could produce WC/Co coatings. In the current investigation, however, the very refractory nature of tungsten has lead to particle resolidification during flight, which needs to be improved through plasma parameters, reactor design, or powder size changes. Thus, the co-spraying of W/Co blends may be possible, provided the Co binder remains molten to fuse the W and WC particles together and to create denser and more wear-resistant coatings than those produced in this investigation. It is suggested that improved reactions and denser coatings could be produced if finer W powder particles (1 to 5 μm) with large surface areas were used.

5. Conclusions

An innovative method for producing wear-resistant coatings has been demonstrated. The plasma reactor has been used to produce reactions between metallic powders and reactive gases, creating fine dispersion of carbides in metallic matrices. Specific wear tests, evaluations of alternative materials systems, and evaluations of the need for low-pressure spray conditions are still under investigation. The specific experimental conclusions of this investigation are summarized as follows.

A concentric, tubular reactor can be fitted onto a conventional low-pressure plasma spray gun without being detrimental to the plasma gun performance. Reactive plasma spray synthesis has proven feasible and advantageous in producing, *in situ*, wear-resistant NiCr/TiC and WC coatings. Dense (> 98%), uniform NiCr/TiC reactively sprayed coatings can be produced.

Refractory metals, such as tungsten, require smaller powder sizes or shorter flight times than those tested. The densities of deposits formed from high melting, refractory metal powders, for example W, were lowered by the cooling effects of disassociating CH_4 and C_3H_6 gases injected into the reactor. The plasma decomposition of these carbonaceous gases required energy, which quenches and reduces the jet temperature. Higher carbonaceous gas flow rates absorbed more energy and therefore produced cooler jets and consequently higher deposit porosity.

Carbide contents in the deposits were increased by increasing reactive gas flow rates. Microstructures, microhardnesses, and X-ray diffraction analyses demonstrated the formation of TiC, Cr_xC_y and W_xC_{1-x} when powders were plasma sprayed with reactive gases. Oxides, observed via XRD, in the deposits originated from the feedstock powders.

Acknowledgments

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