

Deposition of YSZ Coatings by a High Efficiency DC Plasma Torch

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Abstract

This study reports the use of molecular gases for DC plasma generation. The effect of carbon containing gas mixtures on plasma torch performance and the particle parameters during spraying of yttria stabilized zirconia (YSZ) was studied. It was found that the use of CO₂-CH₄ gas mixture as plasma forming gas greatly increases the torch thermal efficiency to 85%. The coating deposition

efficiency of the torch operating with molecular gases was 63% compared to 50% or less for argon based gas mixtures. Higher particle temperature allows deposition of dense coating with low porosity of 3.5%. The coating structure consists of well defined tetragonal modification of stabilized zirconia

1.0 Introduction

Generally plasma spray torches use argon or argon based mixtures for plasma generation. However, the low thermal conductivity and enthalpy of argon impose limits on the thermal efficiency of the process. These restrictions usually are overcome by adding hydrogen or helium to argon. Molecular gases such as air and nitrogen are used extensively for plasma generation for metal cutting, scrap melting and hazardous waste incineration. Because molecular gases must dissociate before ionization, which requires larger energy input, the plasma enthalpy is higher¹. Specifically, carbon dioxide (CO₂) and hydrocarbon (such as CH₄) mixtures have a number of advantages over Ar-based mixtures. Hydrocarbons are fully dissociated at temperatures above 900 °C on hydrogen and carbon. Thermal conductivity of the plasma of CO₂+CH₄ mixture is much higher due to the presence of hydrogen, leading to higher spray process efficiency and improved heat transfer to the sprayed particles. In addition, carbon ionization at arc condition generates an ionic current toward the cathode where carbon ions form an emitting surface of the cathode. Sufficient ionic current from the plasma gas can compensate the carbon sublimation from the cathode resulting in longer cathode life². When appropriate process parameters are established, a dynamic equilibrium between carbon evaporation and precipitation on the cathode could be achieved. The process of carbon ion deposition is fast and the disc shaped deposit 3-4 mm in diameter (Fig.1a) is formed within only a few seconds after the arc has been initiated. The deposit surface has fibrous structure (Fig. 1b) similar to an agglomeration of carbon nanotubes observed during direct current arc discharge in CH₄^{6,7}. High resolution SEM and TEM images (Fig. 1c, Fig. d) have confirmed formation of complex cathode morphology consisting of carbon nanotubes, ropes and carbon nanoparticles.

2.0 Working Gas Properties

It is well-known that the nature of working gas has a great influence on torch performance and heat transfer to particles. Figure 2 compares the temperature dependence of the thermodynamic and transport properties for two gases, Ar and 22%CH₄+78%CO₂ (in volume). Thermodynamic properties of CH₄+CO₂, such as enthalpy, specific heat and density may be calculated relatively simply once the composition is known, using the mass, enthalpy and number density of each species present. The equilibrium composition calculation was based on the mass action law. The transport properties of CH₄+CO₂ were computed from Boltzmann kinetic

theory details of the calculations were presented elsewhere³.

The dissociation and ionization phenomena make a large contribution to energy transport and form the peaks in the thermal conductivity curve (Fig.2a). The specific enthalpy was computed from the electron enthalpy, heavy particle enthalpy and chemical reaction enthalpy. The heavy particle enthalpy dominates at low temperatures and the contributions by chemical reactions become important at high temperatures (Fig. 2b). The specific heat of CO₂+CH₄ exhibits three peaks (Fig.2d) corresponding to the dissociation of molecules at 3500K, the first ionization at 7500K, and the second ionization close to 15000K.

Results show that the enthalpy of CH₄+CO₂ is much higher than that of Ar because molecular gases must dissociate before ionization. It requires larger energy input thus increasing enthalpy of the plasma. For instance, the enthalpy of CH₄+CO₂ is 290% higher than that of Ar at the temperature of 15000K. In Fig 2.d, it is noticeable that the thermal conductivity of CH₄+CO₂ is much higher than that of Ar in the temperature range of 5000-10000K. For instance, at the temperature of 7000K, the value of thermal conductivity of CH₄+CO₂ is 19 times of that of Ar. Since this is the characteristic temperature of plasma jet, it is evident that CH₄+CO₂ could greatly increase heat transfer to sprayed particles.

3.0 Experimental

The torch used for the coating application was developed at Centre for Advanced Coating Technologies (CACT) University of Toronto and operates with CO₂+CH₄ gas mixture (Fig. 3). Important feature of the torch is a water-cooled highly structured graphite cathode. The torch has a cylindrical nozzle 7 mm in diameter and a vortex injection of the plasma gas mixture. Typical arc voltage for the torch is 130-220V in comparison with 45-60 V for Ar+H₂ mixtures. This allows the torch to generate equal power at much lower arc current which reduces thermal load on electrodes and extend their lives.

Measurements of the in-flight particle conditions were made by a DPV-2000 monitoring system (Tecnar Automation Ltd., St-Bruno, Canada). Cross-sections through the sprayed coatings were polished and examined under a scanning electron microscope. The sprayed YSZ powder was Amperit 825-0 (H.C. Starck, Goslar, Germany) with +5/-25 μm particle size distribution. Powder feed rate was 0.5kg/hr.

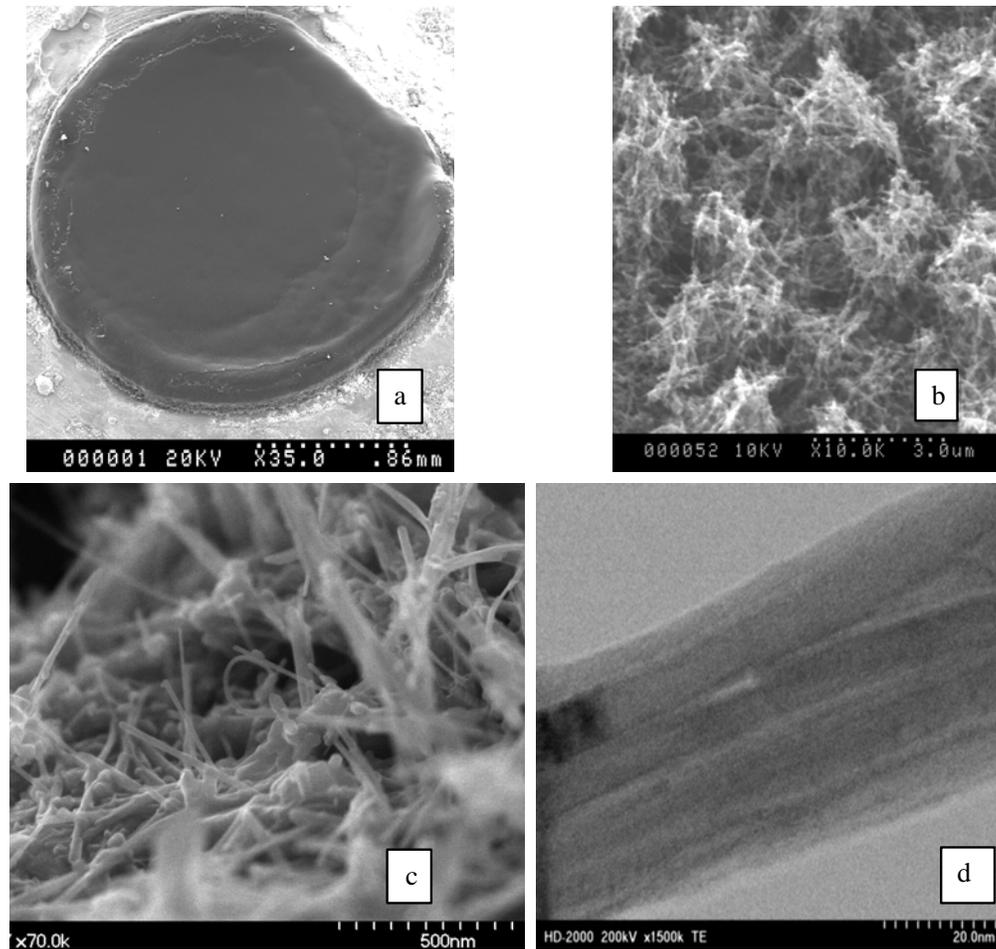


Fig. 1: Carbon deposit (a) and its surface structure at (b) x10K , (c) x70K magnifications and (d)TEM image of carbon nanotubes

4.0 Results

Table 1 presents the comparative results of the influence of three plasma forming gases on the process thermal efficiency. In this comparison two materials were used for cathodes, i.e., tungsten with Ar mixtures and graphite with highly ordered structure with CO_2+CH_4 . During the experiments the same torch and anode were used; only the cathodes varied.

These measurements have confirmed that the torch operating with CO_2+CH_4 gas mixture provides great power and efficiency advantages in comparison with Ar based mixtures. The current torch design allows operation at up to 80 kW input power with average 80% thermal efficiency. Higher thermal conductivity and efficiency of the CH_4+CO_2 plasma provide favorable spraying conditions; it is beneficial to the particle temperature in particular (Fig. 4). The results demonstrate that the particle temperatures were above the melting point of zirconia ($T_m=2700\text{ C}$)

through all tested torch currents even as low as 150A. At the same time particle velocities were similar to the velocities usually obtained using industrial torches.

The particle temperature variation with sprayed distance using CACT torch at 40 and 62 kW power input is shown in Fig. 5. The particles remained molten up to 100 mm spray distance. Whereas the particles sprayed by an industrial SG-100 (Praxair, Concord, NH, USA) torch operating at 41 kW with Ar + 20% He gas mixture were below melting point temperatures just at 50 mm spray distance.

Higher particle temperature is a crucial parameter for producing dense, high quality coatings with high deposition rate. Deposition efficiency (DE) which is a ratio of masses of the deposited coating and feedstock material introduced into the torch. For any thermal spray process it is important to attain maximum DE in order to lower the cost and time of the process. The YSZ was sprayed on aluminium cylinder 180mm in diameter. During spraying the

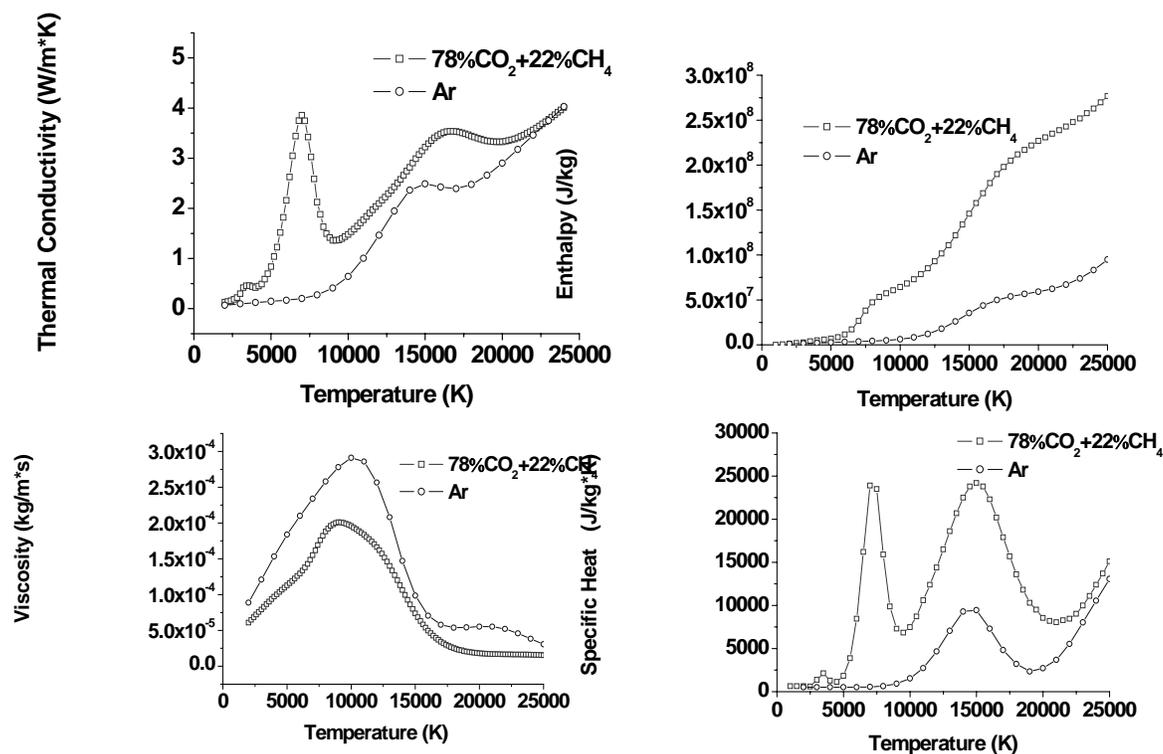


Fig. 2: Properties of Ar and CH₄+CO₂ plasmas: (a) Thermal conductivity, (b) Enthalpy, (c) Viscosity and (d) Specific heat

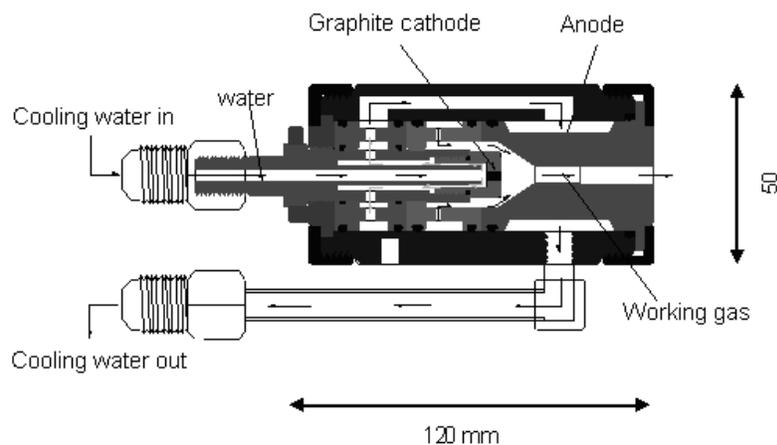


Fig. 3: Schematic of the plasma torch

cylinder surface was cooled by compressed air. While the torch was operated at power range of 42 kW at spray distance 75 mm, the deposition efficiency was 63% at powder feed rate 10.5 g/min. It is known that industrial type torches operating on Ar based mixtures have deposition efficiency 25-50%⁵.

The YSZ coatings deposited by the new torch have a dense microstructure (Fig. 5). Significant overheating of the particles sprayed using CO₂+CH₄

gases greatly increases number of fully molten particles thus positively affecting the coating porosity.

The porosity was measured by image analysis software by examining the coating polished cross section, average value of porosity was 3.5% (Fig. 6). Typical porosity values reported for YSZ coatings deposited by industrial torches were in a range of 8.5-17%^{8, 9}.

Table 1: Torch thermal efficiency operating with various plasma gases

Gas (flow rate)	Cathode material	Arc Current A	Arc Voltage V	Power, kW	Heat flow into plasma kW	Thermal efficiency %
CO ₂ +CH ₄ (75 lpm)	C	265	229	60.2	51.5	85.5
CO ₂ +CH ₄ (45 lpm)	C	265	158	41.9	32.1	76.6
Argon (50 lpm)	W	600	36	21.6	5.7	26.3
Argon + 10% H ₂ (52 lpm)	W	625	49	30.6	9.8	32

YSZ particle T and V at 50 mm

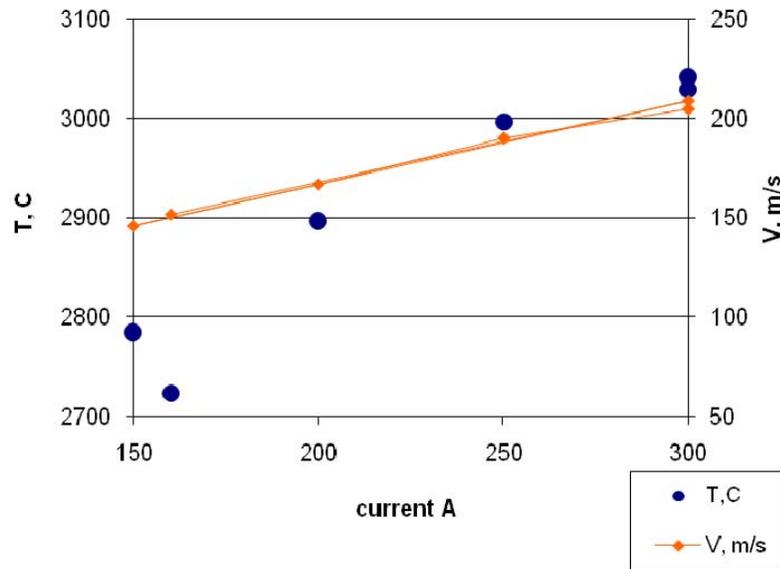


Fig. 4: Particle conditions at 50 mm spray distance

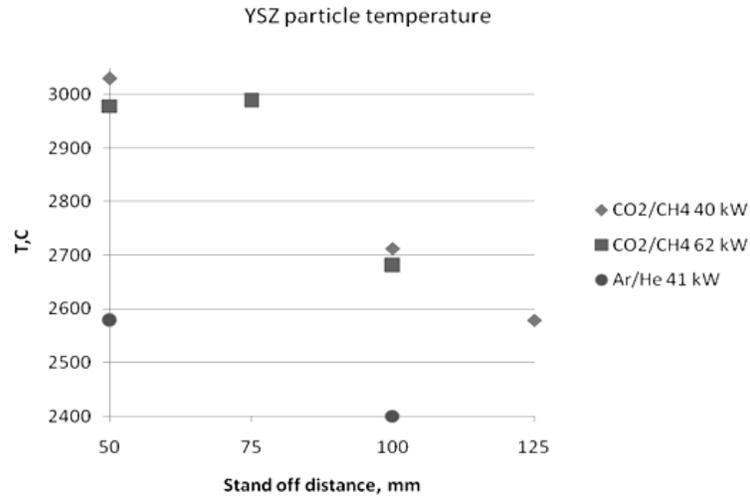


Fig. 5: YSZ particle temperature variations along spray distance for CO₂+CH₄ and Ar+He gas mixtures

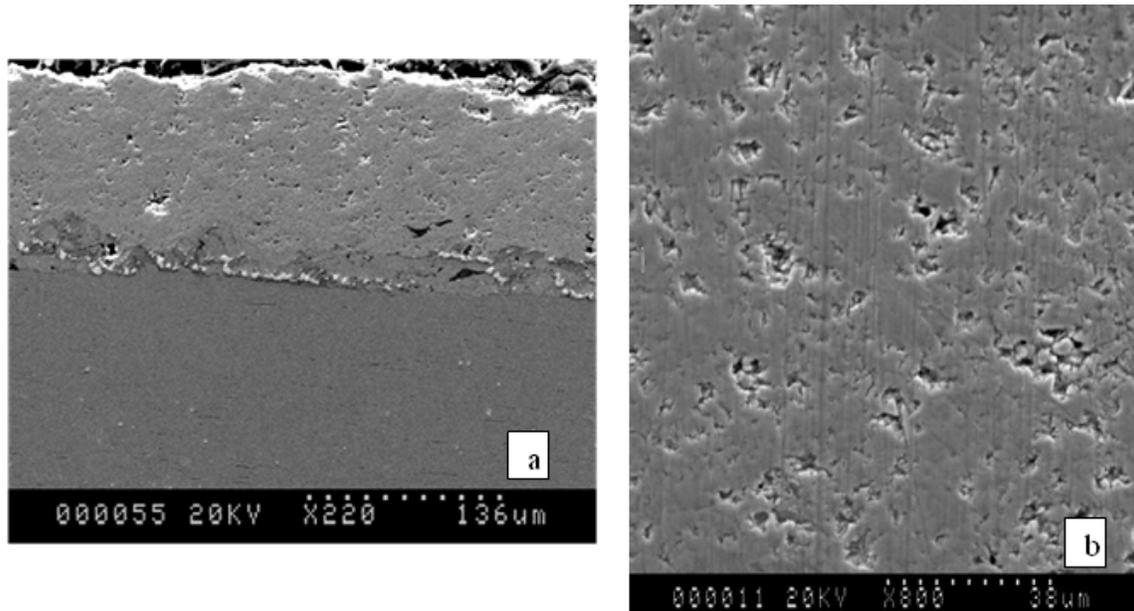


Fig. 6: SEM images of YSZ coating deposited by CACT torch at 75 mm spray distance, (a) YSZ top coat and bond coat x220, (b) YSZ top coating , x800

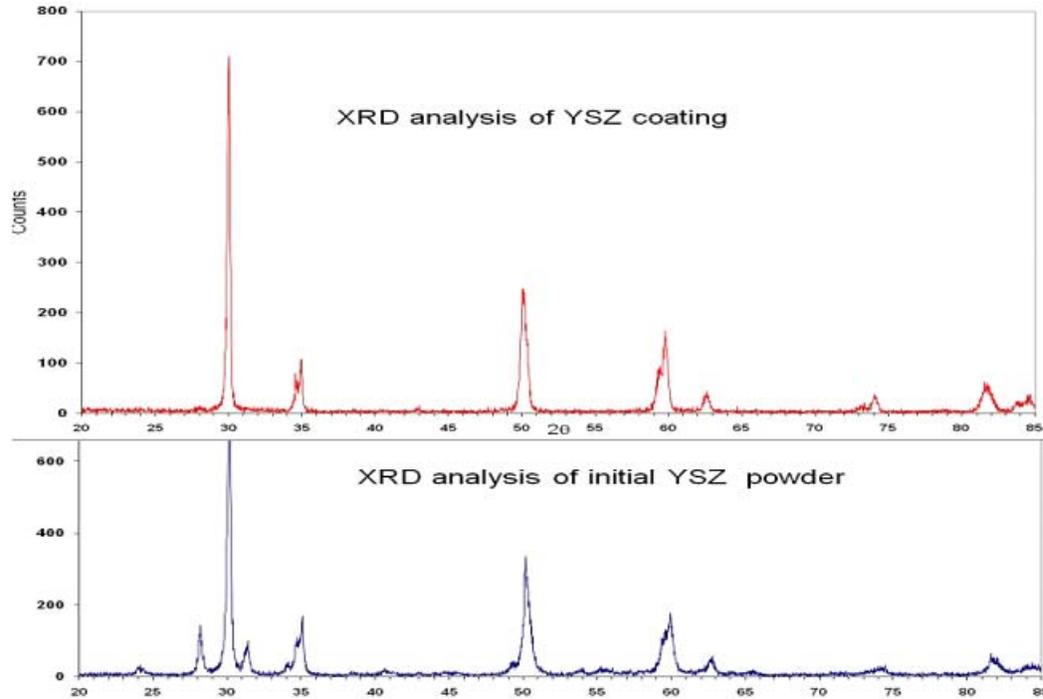


Fig. 7: XRD of coating

X-ray diffraction analysis of the coating (Fig.7) shows well defined tetragonal structure of stabilized zirconia and just a trace of cubic phase. Whereas the initial powder spectra have peaks of monoclinic phase. The coating phase composition is similar to the coating deposited by a torch operating at 45 kW input power with Ar+H₂ plasma gas¹⁰.

5.0 Conclusions

1. Experimental results show that using molecular gases such as CO₂+CH₄ can effectively increase the torch power and plasma jet enthalpy.
2. The thermal efficiency of the torch was up to 85%.The torch current design allows it operates consistently in power range of 30-80 kW.
3. The influence of the plasma gas composition on the in-flight particle conditions also was studied. Particle temperature is up to 400 °C higher compare to the particles sprayed in Ar+He mixture.
4. With the results presented, it is possible to conclude that the new torch is more efficient heater than torches operating with argon, which positively affects the coating deposition efficiency and porosity.
5. Use of inexpensive gases and higher deposition efficiency make spray process more economically efficient.

6.0 References

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