JTTEE5 17:608–611
DOI: 10.1007/s11666-008-9265-2
1059-9630/$19.00 © ASM International

Technical Note

# Plasma Spraying of Metal Coatings Using $CO_2$-Based Gas Mixtures

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(Submitted May 16, 2008; in revised form September 29, 2008)

**Compared to argon, plasmas generated by molecular gases and operated at the same electric current level contain much higher enthalpy. This is because molecular gases must dissociate before ionization, which requires larger energy input. The authors have developed a new DC plasma torch, which operates with a mixture of carbon dioxide ($CO_2$) and methane ($CH_4$). The torch was employed for plasma spray coating with input power in a range of 30 to 45 kW. This paper reports on the effect of $CO_2$/$CH_4$ mixtures on the particle conditions during spraying of nickel alloy powders. Results of gas composition analysis at various distances from the nozzle exit are presented. The particle in-flight conditions, coating microstructure, and deposition efficiency are analyzed.**

**Keywords** coating oxidation, graphite cathode, molecular gases plasma, plasma composition

## 1. Introduction

Molecular gases are commonly used for high power plasma generation in waste or coal gasification and in steelmaking. In comparison with inert gases, the higher energy that is required for dissociation and ionization of the molecular gases translates into a higher plasma enthalpy. High plasma enthalpy is desirable as it allows higher material feed rate and higher materials processing rates. Carbon-containing molecular gases, in particular a mixture of carbon dioxide and hydrocarbons, have a number of advantages. In addition to high plasma enthalpy, such plasmas have high thermal conductivity resulting in efficient heat transfer to treated materials. For example, at one atmosphere pressure and a temperature of 7000 K, the thermal conductivity of mixture containing two parts $CO_2$ and one part $CH_4$, is almost 20 times greater than that of argon (Ref 1, 2).

This article is an invited paper selected from presentations at the 2008 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Thermal Spray Crossing Borders, Proceedings of the 2008 International Thermal Spray Conference*, Maastricht, The Netherlands, June 2-4, 2008, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2008.

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Another feature of carbon-containing plasma gases, which was exploited in the design of the torch in this study, is as follows. Positive carbon ions are produced in the arc region, and because of the Coulomb attractive forces they flow toward the negatively charged cathode and deposit on its surface. The formation of a complex surface morphology of the deposit, which consisted of carbon nanotubes and nanoparticles, has already been reported in a previous publication (Ref 3). If the cathode is made of graphite, the induced ionic current could partially or totally compensate for the sublimation and loss of the cathode material, which occurs due to high cathode heat fluxes. This phenomenon may then greatly increase the cathode life (Ref 3, 4).

Based on the above principle, a new DC plasma torch with graphite cathode for thermal spraying was designed, constructed, and tested at the *Centre for Advanced Coating Technologies* (CACT). Because the arc voltage is relatively high (130-220 V), it was able to generate a high power plasma at much lower arc currents in comparison with conventional argon mixtures. Lower arc current is beneficial as it considerably reduces the thermal load on the electrodes, resulting in longer electrode life. The torch was operated in a power range of 20 to 70 kW at arc currents that were no more than 400 A. The thermal efficiency was measured and was found to be high (60-85%). This paper presents the effect of the volumetric ratio of $CO_2$ to $CH_4$ on the plasma plume composition and on the particle parameters during spraying of Ni alloy powder.

## 2. Experiment

The new torch used for the coating application is operated with $CO_2$/$CH_4$ gas mixtures. One important feature of the torch is a water-cooled, button type cathode made of a highly structured graphite. The torch has a cylindrical anode with 7 mm in diameter and a vortex gas distributor, and the powder is externally injected (Ref 3).

**Table 1 Torch operating conditions and thermal efficiency (measured)**

| Gas flow | Cathode material | Current, A | Voltage, V | Power, kW | Thermal efficiency, % |
|---|---|---|---|---|---|
| $CO_2 + 17\%CH_4$ (30 lpm) | C | 305 | 138 | 42.1 | 65 |
| $CO_2 + 30\%CH_4$ (30 lpm) | C | 310 | 132 | 40.9 | 60 |
| Ar (55 lpm) | W | 600 | 47 | 28.2 | 35 |

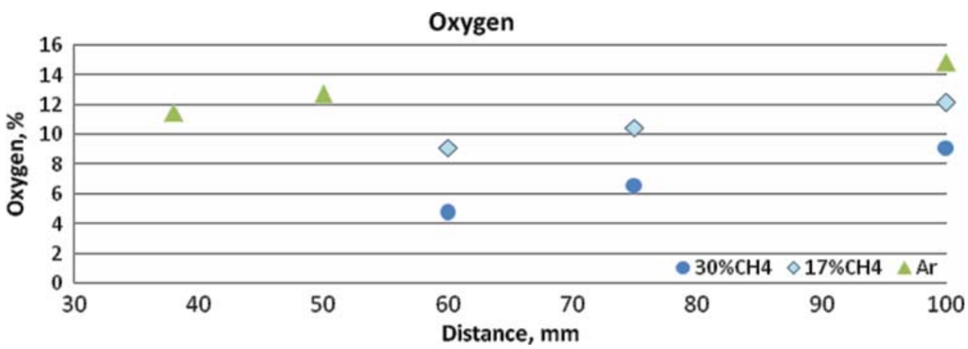


**Fig. 1** Oxygen content variation along the torch axis for $CO_2$ with 30% and 17%$CH_4$ gas mixtures and Ar

Two gas compositions were considered with 17 and 30% volumetric $CH_4$ content; the total gas flow rate was, however, kept constant at 30 lpm. For comparison, the torch was also operated with argon. In this case the graphite cathode was changed and tungsten was used as cathode materials. Table 1 shows the torch operating conditions used in this study.

The gas composition in the plasma jet was measured by a mass-spectrometer (Microvision Plus from MKS Instrument, Crewe, UK) attached to a water cooled Pitot probe. The probe tip was placed along the torch centerline at distances of 60, 75, and 100 mm. To prevent overheating of the probe, the closest distance to the torch exit was limited to 60 mm. In contrast, when argon was used as plasma gas, the minimum distance was 40 mm.

The sprayed Ni-based alloy powder was Metco 461NS (Sulzer-Metco, Westbury, NY, US) with particle size distribution of $-150+22$ μm. Powder feed rate was 14 g/min; the relatively low feed rate was limited by the powder deposition inside the nozzle for SG-100 torch. Measurements of the in-flight particle conditions were made by a DPV-2000 monitoring system (Tecnar Automation, St-Bruno, QC, Canada). Cross sections through the sprayed coatings were polished and examined under a scanning electron microscope (SEM). Oxygen concentrations of the initial powder and coatings were measured using a LECO TC-136 (Leco, St-Joseph, MI, USA) oxygen analyzer.

## 3. Results and Discussion

### 3.1 Gas Composition

Plasma spray process in the ambient atmosphere is always accompanied by entrainment of air into the plasma plume, which intensifies in-flight metal particle oxidation. It is important to know oxygen content of the plasma specifically for the noninert carbon dioxide gas mixtures. Results of the measurements showed that the oxygen content was much lower for $CO_2/CH_4$ plasma at a distance of 60 mm in comparison with argon plasma at a distance of 50 mm (Fig. 1). As expected, the mixture with higher methane content, i.e., with 30%$CH_4$, had a lower concentration of oxygen, approximately one-third of that for Ar plume at 60 mm distance.

Farther from the torch exit, in spite of strong air entrainment, the oxygen level remains significantly lower for $CO_2/CH_4$ mixtures. For instance, at a distance of 100 mm the oxygen concentration for the mixture with 30%$CH_4$ and for pure argon plasma was 9 and 14.9%, respectively. It is important to note that in addition to lower oxygen content, $CO_2/CH_4$ plume contains a significant amount of CO. The presence of CO may be the reason for lower oxygen content in the $CO_2/CH_4$ plasma, since the entrained oxygen may react with CO and produce $CO_2$. The gas chemistry in the plume is thus very advantageous as it reduces the possibility of in-flight oxidation of the powder (Fig. 2). At 60 mm distance, for the methane-rich mixture, the measurements also showed the presence of hydrocarbons (1.6%) and hydrogen (0.7%).

### 3.2 Particles Conditions

The design of the CACT torch and its cooling capacity does not allow operating the torch at currents above 450 A. For comparison, the SG-100 (Praxair, Concord, NH, USA) torch for coating applications in pure argon was used. SG-100 was operated at a similar input power, which required an arc current of 700 A. The argon flow rate was 55 lpm. Earlier results have proved that the thermal properties of plasma generated by $CO_2/CH_4$ mixture are much better than argon plasma and that

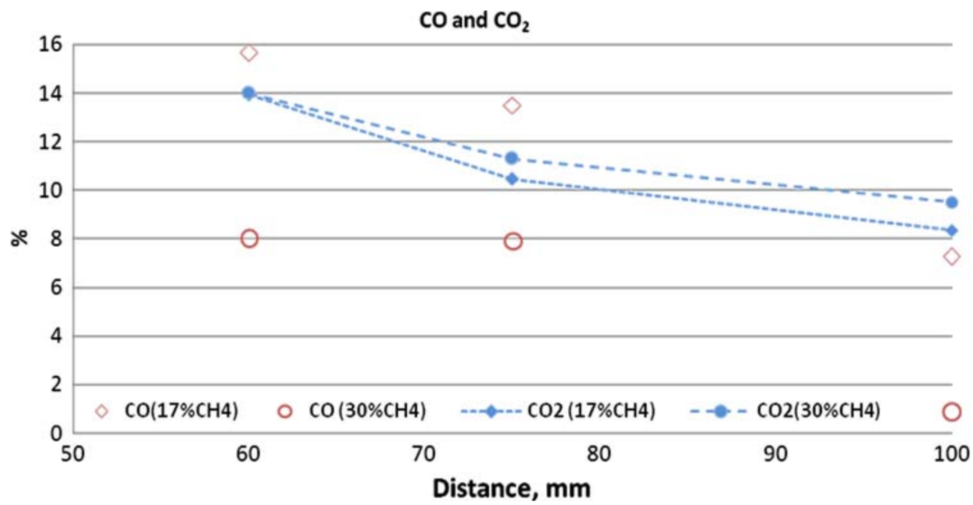


**Fig. 2** CO and $CO_2$ content in plasma plume along the torch axis for $CO_2$ with 30% and 17%$CH_4$ gas mixtures

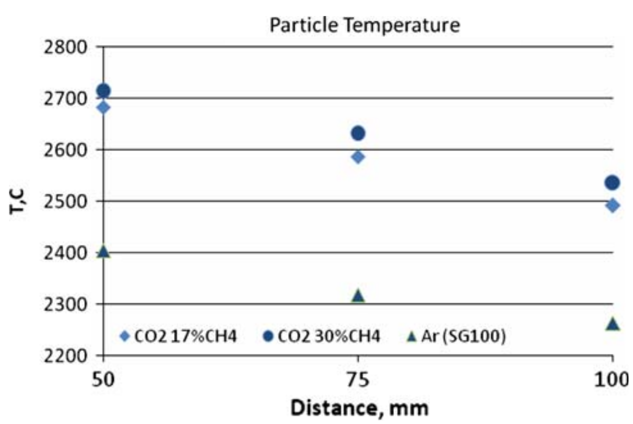


**Fig. 3** Particle in flight temperature evolution

injected powders are heated and melted much more effectively (Ref 1, 3). The results of measurements (Fig. 3) demonstrate that the particle temperatures at all spray distances were about 300 °C above of the particles temperature sprayed in Ar despite internal powder injection in SG-100 torch as against the external injection of the powders in this study. It is worth noting that higher methane results in higher hydrogen concentration, which in turn increases the thermal conductivity of the plasma (Ref 2). Effect of these conditions could be seen in higher particle temperatures for the mixture with 30%$CH_4$.

Particle velocities along spray were very close for both torches. The velocities between 50 and 100 mm spray distances decreased from 175 to 96 m/s for the SG-100 torch and from 155 to 109 m/s for the new torch.

Deposition efficiency of the spray is an important parameter as it affects the operating cost. To improve deposition efficiency, it is important to achieve a high degree of melting of the injected powders. To measure the degree of melting, a scan of the plasma plume was performed by DPV-2000 at 9 × 9 points with 3 mm step after

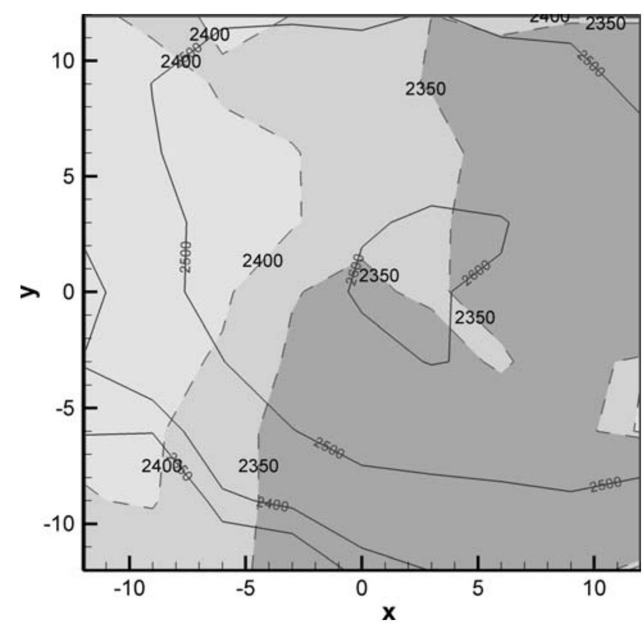


**Fig. 4** Particle temperatures at 75 mm spray distance sprayed in mixture with 17%$CH_4$ (solid lines) and Ar (shaded area on background)

"*auto centering*" routine at all spray distances. This gives an opportunity to compare particle conditions not only along the centerline but also within the cross section of the jet. Figure 4 shows a map of particle temperature distribution at 75 mm distance for 83%$CO_2$ + 17%$CH_4$ and for argon plasmas.

The shaded area with dash lines on the background of Fig. 4 represent the particles temperature distribution sprayed in Ar, whereas solid lines show isotherms for particles sprayed with 83%$CO_2$ + 17%$CH_4$ gas mixture. These measurements demonstrate that, with the new torch, a significantly larger number of particles were heated to higher temperatures. In any thermal spray

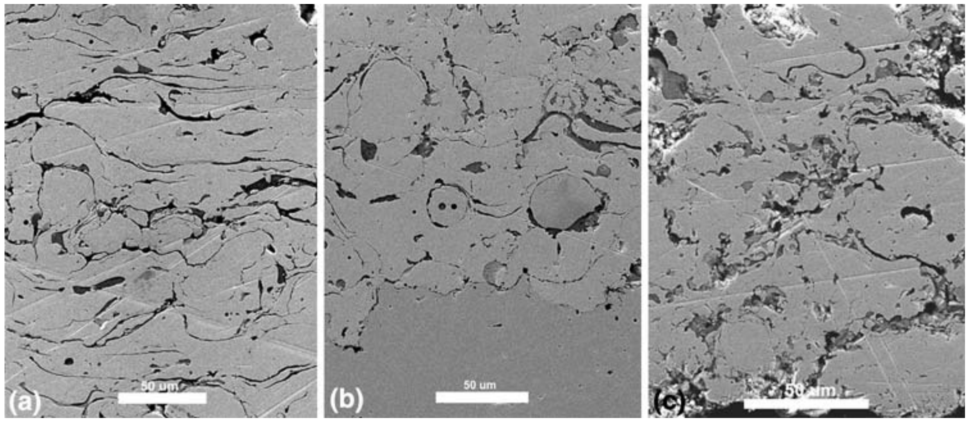


**Fig.5** Micrographs of the coatings deposited at 75 mm distance in mixtures with 30% $CH_4$ (a), 17% $CH_4$ (b), and Ar (c)

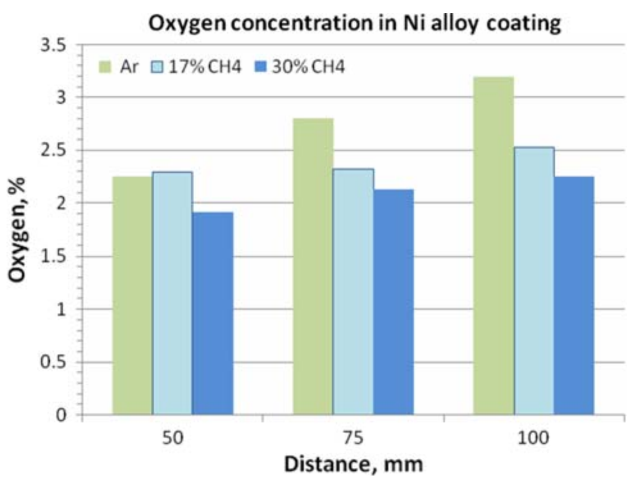


**Fig. 6** Oxygen content measured in deposited coatings

process, it is important to attain the maximum deposition efficiency to lower the cost and time of the process. It should be noted that, to improve particle heating, SG-100 typically operates with the addition of an auxiliary gas such as $H_2$ or He.

A large number of molten particles at spray distance will result not only in higher deposition efficiency but also in producing dense, better quality coatings. The thickness of the coatings per pass of the plasma torch with a traverse velocity of 10 m/min at 50 mm standoff distance was measured. For the 70% $CO_2$ + 30% $CH_4$ composition, the deposit thickness per pass was approximately 40 μm; the thickness was 33 μm for the mixture with 17% $CH_4$ and 11 μm for Ar.

Metallographic observations of the deposited coatings also revealed positive effect of higher thermal properties of $CO_2/CH_4$ plasma on the coating microstructure (Fig. 5). The coatings have lamellar structure with porosity of 9.8% (Fig. 5a) and 10% (Fig. 5b). For porosity measurements, image analysis software Clemex Application Suite was used. It is worth noting that the large particles of initial powder (up to 150 μm) were molten or softened enough to be deposited and form flattened lamellae. The coatings had well-adhered interface.

The coating deposited by argon plasma (Fig. 5c) was formed by less-flattened particles with extensive inter lamellar porosity of 12.4%, which is indicative of insufficient melting. Adhesion of the coating was poor, which resulted in delamination during deposition.

Oxygen concentration of the deposited coatings accurately reflects differences in the plasma plume composition (Fig. 6). Higher oxygen content of Ar plasma resulted in a more in-flight oxidation of the powder. The particles oxidation deposited by the CACT torch is much lower despite higher particle temperatures during deposition. Oxygen content in the feedstock powder was measured at 2.43% mass.

## 4. Conclusions

The new torch operating with a $CO_2/CH_4$ mixture generates a plasma plume, which creates favorable conditions for spraying metals due to lower oxygen level and the presence of reducing gases.

Better thermal properties of the $CO_2$-based mixtures produced dense well-adhered coatings from powders with relatively large particle size and at about three times higher deposition rate than in argon plasma.

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