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In-flight oxidation of iron particles sprayed using gas and water stabilized plasma torch

G. Espie[a], A. Denoirjean[a,*], P. Fauchais[a], J.C. Labbe[a], J. Dubsky[b], O. Schneeweiss[c], K. Volenik[b]

[a]*SPCTS UMR CNRS 6638, 123 Avenue Albert Thomas 87060 Limoges CEDEX, France*
[b]*Institute of Plasma Physics, ASCR, Za Slovankou 3, 182 21 Praha 8, Czech Republic*
[c]*Institute of Physical Metallurgy, ASCR, Žižkova 22, 616 62, Brno, Czech Republic*

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Abstract

This paper is devoted to the study of the oxidation of iron (low carbon) particles during their flight in d.c. plasma jets flowing in air as well as the oxidation after the impact and solidification of particles onto the substrate. Two types of torches have been studied: a conventional one: gas stabilized plasma (GPS) with an effective power P_{eff}=18 kW and a more exotic one: water stabilized plasma (WSP) with P_{eff}=139 kW. Besides their power levels, their main difference lies in the plasma gas specific mass downstream of the anode attachment almost 10 times lower in GSP than in WSP with correspondingly the plasma temperature 10,000 K higher for WSP. The GSP oxidation is promoted by the convective movement induced within the liquid metal droplets by the plasma flow in the jet core. In-fight oxidation shows strong similarities for both techniques with mainly the formation of non-stoichiometric Fe_xO. In contrast in coatings depending on the temperature during spraying, Fe_2O_3 or Fe_3O_4 are observed.

Keywords: In-flight oxidation; Gas stabilized plasma; Water stabilized plasma

1. Introduction

During the last 30 years, studies in plasma spray coatings have evolved from a semi-empirical approach to a more scientific one accounting, as much as possible, for all parameters involved in the process [1,2]. Nowadays, many studies, both experimental and theoretical, have allowed establishing correlations between spraying conditions and coating properties [3,4]. In addition, recent studies highlight the interaction between injected particles and plasma jets. In case of atmospheric plasma spraying (APS) with either a gas stabilized plasma (GSP) or a water stabilized one (WSP), because of the very high velocities of the exiting plasma jets and arc root fluctuations, both inducing large scale eddies in jet fringes, air and thus oxygen is entrained into plasma jet cores [5–7]. This air entrainment process, which is of engulfment type [7], together with the high temperatures encountered in plasma jets, result in oxidation of metallic particles injected. Thus, the in-flight oxidation of particles changes their composition prior to their impact onto the substrate and modifies their melting properties. Splats formation and layering is thus different from that of pure metal and correspondingly coating properties are also modified. During its formation, the coating is swept by hot gases of the plasma plume. Splat oxidation can be neglected because each splat is covered by the next one within 10–20 µs, while a few seconds occur between two successive passes. Thus, the corresponding oxidation will

Abbreviations: APS, atmospheric plasma spraying; CEMS, conversion electron Mössbauer spectroscopy; d.c., direct current; EDS, energy dispersion spectroscopy; GSP, gas stabilized plasma; i.d., internal diameter; LECO, global oxygen content analysis; MS, Mössbauer spectroscopy; P_{eff}, effective power in the plasma jet; SEM, scanning electron microscopy; WSP, water stabilized plasma; XRD, X-ray diffraction.

* Corresponding author. Tel.: +33 5 55 45 74 38; fax: +33 5 55 45 72 11.
E-mail address: alain.denoirjean@unilim.fr (A. Denoirjean).

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Nomenclature

a	lattice parameter (nm)
B_{hf}	hyperfine induction (kG)
d_p	diameter of sprayed particles (m)
g	index related to plasma gas
p	index related to particles
Re^p	Reynolds number related to the in-flight particle: $Re^p = \rho\ u_r d_p/\mu$ (−)
u_r	relative velocity gas-particle (m/s)
x	iron stoichiometry in iron oxides
z	axial distance downstream of the nozzle exit (mm)
ΔE_q	quadruple splitting (mm/s)
$\Gamma/2$	line width (mm/s)
δ	isomer shift (mm/s)
μ	dynamic viscosity (Pa s)
v	kinematics' viscosity ($v=\mu/\rho$) (m^2/s)
ρ	specific mass (kg/m^3)

be closely linked to the mean temperature at which the coating can be kept during spraying. These two oxidation steps result in lower mechanical properties (especially coating ductility), and corrosion resistance, of metallic coatings. The aim of this work is to understand the different oxidation phenomena in order to limit them when spraying in air atmosphere. For that, it is necessary to determine the respective importance of in-flight oxidation as well as that during coating formation. The former can be limited by shrouding either with a combustible gas consuming part of the oxygen which could be entrained within the plasma or by a water cooled shroud. The latter depends mainly on the coating mean temperature during spraying, which can be controlled by air cooling devices. Of course, the coating and substrate have to be kept over the transition temperature (temperature over which adsorbates and condensates are desorbed) in order to achieve a good coating adhesion/cohesion.

The oxidation was studied by spraying of a "pure" iron powder, although it is useless for plasma spraying applications. The reason was the simple composition of the metal and its oxides, which makes easier the interpretation of results. This paper proposes a comparison of the oxidation results obtained when spraying pure iron by two plasma spray processes: GSP and water stabilized plasma (WSP) working with very different power levels (almost one order of magnitude difference and different plasma forming gases (Ar/H_2 or water)).

The main characteristics of the two plasma jets employed, the set-ups to collect the in-flight particles and a comparison of the in-flight formed oxides in both processes are presented. A description of oxides in coatings is also given and results are discussed.

2. Experimental

2.1. Plasma torches

2.1.1. Gas stabilized plasma

In a gas stabilized d.c. plasma torch, the plasma jet is produced inside the anode nozzle by the plasma forming gas flowing through the arc striking between the thoriated tungsten cathode tip and the anode. In plasma spraying in most cases, Ar–He, $Ar–H_2$ or $N_2–H_2$ mixtures are used to provide enough enthalpy and a sufficient heat transfer to melt particles which is not the case with pure Ar. It has been chosen to work with an $Ar–H_2$ mixture. In conventional working conditions and with an anode nozzle 7 mm i.d., the plasma jet exits the nozzle at velocities as high as 1000 and 2000 m/s [8] and with temperatures around 13,000–14,000 K [9,10]. This high velocity creates an important shear stress at the nozzle exit resulting in the formation of vortex rings, which coalesce further downstream leading to the engulfment of cold and dense bubbles of air [11]. This engulfment process is also promoted by the piston flow induced by the arc root fluctuations, especially in the restrike mode obtained with diatomic gases [1]. The composition of the plasma–air mixture depends strongly on the jet exit velocity in terms related to the plasma forming gases used, their total mass flow rate, the arc current intensity and the nozzle internal diameter. The mixing of air with the plasma jet induces a fast decrease of the velocity and temperature of expanding jet (in the first tens of millimeters).

The d.c. plasma gun used was similar to the PT-F4 (commercialized by Sulzer Metco) with a 7-mm internal diameter (i.d.) nozzle. The particles were injected outside the nozzle, 3 mm downstream of its exit with an injector 1.8 mm of i.d. orthogonal to the jet axis and disposed at 7.5 mm from it. The carrier gas flow rate was adjusted in order to achieve a mean trajectory of the particles making an angle of about 4° with the torch axis. The stand-off distance was 100 mm downstream of the nozzle exit. No shrouding was used.

2.1.2. Water stabilized plasma

A high throughput plasma spray deposition system based on WSP was developed in the early 1970s in the Institute of Plasma Physics ASCR in Prague. Water is fed into an especially shaped chamber where it creates a swirl. An electric arc burns between the graphite cathode within the chamber and the rotating anode outside the chamber [12,13]. The electric arc partially evaporated water from the swirl surrounding it. The steam is then converted into ionized medium creating the plasma jet. Feedstock material is introduced into the jet outside the torch. Since for each atom of oxygen in the plasma there are two atoms of hydrogen, the oxidizing power of the plasma as such is balanced. Thus, oxides entrapped within particles during their flight in the plasma are mainly due to the surrounding