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Plasma spray of Ti_2AlC MAX phase powders: Effects of process parameters on coatings' properties

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ABSTRACT

Plasma spraying was employed to spray commercial Ti_2AlC MAX phase powders onto Inconel 600 substrates. Effects of different process parameters, including arc current, flow rates of primary Ar, secondary H_2 and carrier Ar, powder feedrate, spray distance as well as presence of cooling air on the backside on the substrate were systematically screened by evaluating the content of Ti_2AlC in the coating through X-ray diffraction and Rietveld phase analysis. The highest content of the remaining Ti_2AlC in the coating was achieved to be 26.0%. The coating with 26.0 wt% of Ti_2AlC was further analyzed by a variety of techniques to probe its surface chemistry, morphology, cross-sectional microstructure, mechanical properties and salt fog corrosion resistance.

1. Introduction

MAX phase materials are the class of 60 plus ternary carbides and/or nitrides with a general formula of $M_{n+1}AX_n$ (M: an early transition metal, A: a group 12–16 element, X: carbon and/or nitrogen, n = 1–3) [1]. They have attracted considerable interests since mid-1990s due to their unique combinations of metallic and ceramic properties. Like metals, they have good electrical and thermal conductivity, high ductility, good machinability and excellent thermal shock resistance. Like ceramics, they possess low density, high stiffness, high melting points and good oxidation/corrosion resistance. Such exceptional properties arise from the co-existence of the strong covalent-ionic M-X bonds and the weak metallic M-A bonds inside the layered hexagonal structure (space group $P6_3/mmc$) of MAX materials, which are constructed by repeating a three-layer structure (consisting of two $M_{n+1}X_n$ layers intercalated by one atomic A layer) vertically [1,2]. The weak metallic M-A bonds make it feasible to etch A layers away selectively, leaving the strongly-bonded MX layers behind and creating a new family of 2D materials called MXene in order to emphasize their relationship with the MAX phases and the parallel with graphene [3].

Ti_2AlC, an early-discovered and well-studied MAX phase material, has also processed the dual metallic-ceramic properties including a small density (4.11 g/cm^3), which have led to the exploration of its application in a variety of fields including high temperature protective coatings [4] and radiation-tolerant cladding material for the nuclear power plants [5,6]. After bulk [7] and thin films [8–12] Ti_2AlC have been synthesized in various laboratories, commercial Ti_2AlC MAX phase material in bulk (bar, cylinder, plate, rod & tubes) [13–15] and powder [6,16–21] forms have been produced and tested. Despite of minority phases presence such as Ti_3AlC_2, TiC and TiAl [6,14–20], the availability of such commercial Ti_2AlC materials, especially in powder form, has promoted the exploration of its potential applications in various industries including aerospace, nuclear plant, marine and offshore as thick coatings using two thermal spray techniques, high-velocity-oxy-fuel (HVOF) spray [16–19] and cold spray [6,20,22].

During HVOF spray process, the temperature in the center of flame (>2100 °C, [18]) is significantly higher than the decomposition temperature of bulk Ti_2AlC (1400 °C, [15]). Despite a short dwell time of a few milliseconds in the plasma, the Ti_2AlC MAX phase powders are still partially melted and softened by the thermal energy. At the same time, they are accelerated by the kinetic energy to impact the substrate surface, deform, recrystallize, solidify and finally cool down. Thus, although the coatings sprayed by HVOF were dense and had good adhesion to the stainless steel substrates, Ti_2AlC phase present in powders decomposed into a mixture of TiC, Ti_3AlC_2 and Al_xTi_y phases in such coatings [16,18]. The intensity of TiC(111) peak around 36.2° in the XRD patterns can serve as an indication of the degree of Ti_2AlC and Ti_3AlC_2 phase decomposition. The higher intensity of TiC(111) peak indicates larger degree of phase decomposition and vice versa. There have been efforts to mitigate the impact of thermal energy on the phase decomposition of the Ti_2AlC MAX phase powders. Increasing Maxthal 211® powder size (d_{50} from

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30.4 μm [18] to 56.3 μm [16,19]) and decreasing gas ($H_2 + O_2$) flow rate (from 953 to 441 L/min [18]) help retain higher amount of Ti_2AlC phase in the final coating, but at the expense of thinner coating with lower cohesion. Annealing such HVOF-sprayed Ti_2AlC coatings at 850 °C at a base pressure of 10^{-3} Pa helped restore Ti_2AlC wt% in the coating partially, due to intercalation of Al into the under-stoichiometric TiC [19]. Recent attempts of spraying using cold spray technique, which utilizes much less thermal energy than HVOF, enabled quite dense and adherent Ti_2AlC coatings. The coatings had much reduced phase decomposition, which can be seen from weak TiC(111) peak in the XRD patterns of the obtained coatings [6,20,22]. However, occurrence of cracks in such coatings is detrimental for reliable coatings [20,22].

Plasma spray is another thermal spray technique [23], which has been widely employed in aerospace maintenance, repair and overhaul for protecting new parts and repairing worn ones, such as to spray thermal barrier coating [24,25]. However, there have been no reports so far to utilize the widely available plasma spray to deposit the Ti_2AlC powders, due to the concerns that very high temperature in the plasma would lead to severe or even complete decomposition of Ti_2AlC powders. Our recent work indeed showed that holding Ti_2AlC Maxthal 211® powders at 1000 °C for 5 h led to their full decomposition associated with oxidation into TiO_2 and Al_2O_3 [26]. Nevertheless, it has been reported that plasma spray can be used to spray a mixture of Ti, SiC and graphite powders, and MAX phase material, Ti_3SiC_2, was synthesized in the coating [27]. Therefore, although the temperature in the center of plasma is very high (12,000–16,000 °C, [23]), it may be still possible to spray the Ti_2AlC powders using plasma spray after optimizing the process parameters, instead of replacing the carrier gas with liquid flow and spraying the MAX phase powders (i.e., Ti_3AlC_2 [28]) using liquid plasma spraying (LPS).

In this work, we thus explored the possibility to spray Ti_2AlC powders using plasma spray by tuning a series of parameters, including arc current, flow rates of primary Ar, secondary H_2 and carrier Ar, powder feedrate, spray distance as well as presence of cooling air on the backside of the substrate. In order to understand qualitatively the effects of various process parameters, we further examined the weight percentage of remaining Ti_2AlC phase in the coatings through X-ray diffraction and Rietveld phase analysis. The coating sprayed under the optimal condition was further analyzed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), optical microscopy, macro-hardness tester, pulling test, three-point bending test, wear test and salt spray test for its surface chemistry, morphology, cross-sectional microstructure, macro-hardness, bond strength, adherence, wear resistance and salt fog corrosion resistance, respectively.

2. Material and methods

Ti_2AlC MAX phase powders (Maxthal 211®) were produced in Sandvik AB Sweden by crushing and sifting bulk Ti_2AlC after combustion synthesis. A large particle size of 45–100 μm was intentionally selected to minimize the oxidation and decomposition drawbacks the small particles encounter when they fly through the hot plasma jet during the spray. Substrates are Inconel 600 coupons (AMS-5540N, 0.1 × 4.45 × 7.62 cm^3), which were cleaned using acetone and followed by grit-blast using Al_2O_3 grit 60 at a pressure of $1.7–2.1 \times 10^5$ Pa, prior to the spray. As measured by the surface profiler (KLA Tencor® P-16 plus), the R_a (arithmetic average roughness) and R_t (peak to valley in the roughness profile across median size splats) of the substrates after grit blasting were increased from 295.3 nm and 3.6 μm to 4.6 μm and 31.3 μm, respectively. The substrates were mounted vertically on a carousel without rotation. The plasma spray was performed using an Oerlikon Metco 9MC plasma spray system with Ar and H_2 gas mixture. Powders were dried at 60 °C in an oven for a minimum of 2 h, and fed vertically by a twin-10 powder feeder using N_2 as carrier gas at the exit of a F4MB spray gun, which has a nozzle diameter of 6 mm (Fig. 1(a)). The color of the plasma jet was visually inspected through the window in the spray booth and was ensured to be uniform after the powders were injected by the feeder into the plasma jet. During the spray, the gun was held horizontally and traversed back and forth across sample surface with a pass spacing of 4 mm. The movement of the spray gun in one pass is illustrated in Fig. 1(b). At the end of spray, the gun will move directly to the starting point and spray the next pass by repeating the same movement path. Substrates were pre-heated by one pass prior to spray to eliminate any remaining water/adsorbate on the surface and to improve the bonding properties. Parameters including arc current, flow rates of primary Ar and secondary H_2 gases, powder feedrate, spray distance, carrier Ar flow rate and presence of substrate cooling were systematically tuned (Fig. 1(a)). The crystalline structures of the resulting coatings were analyzed using Bruker general area detector diffraction system (GADDS) XRD operating at a voltage of 40 kV and a current of 40 mA (Cu Kα X-ray, $\lambda = 1.54$ Å). The different phases' relative weight percentages were subsequently determined by Rietveld phase analysis using TOPAS software. The surface chemistry, morphology and microstructure of the optimum coating were analyzed by XPS (Thermo Fisher Scientific Theta Probe System), SEM (JEOL FESEM 7600F) equipped with energy dispersive spectroscopy (EDS) (Oxford Aztec Synergy System) and optical microscope (Olympus BX60). XPS spectral deconvolution was achieved by a curve-fitting procedure based on Lorentzians broadened by a Gaussian function, due to the instrumental resolution, using the manufacturer's standard software (Avantage ®). Component peak

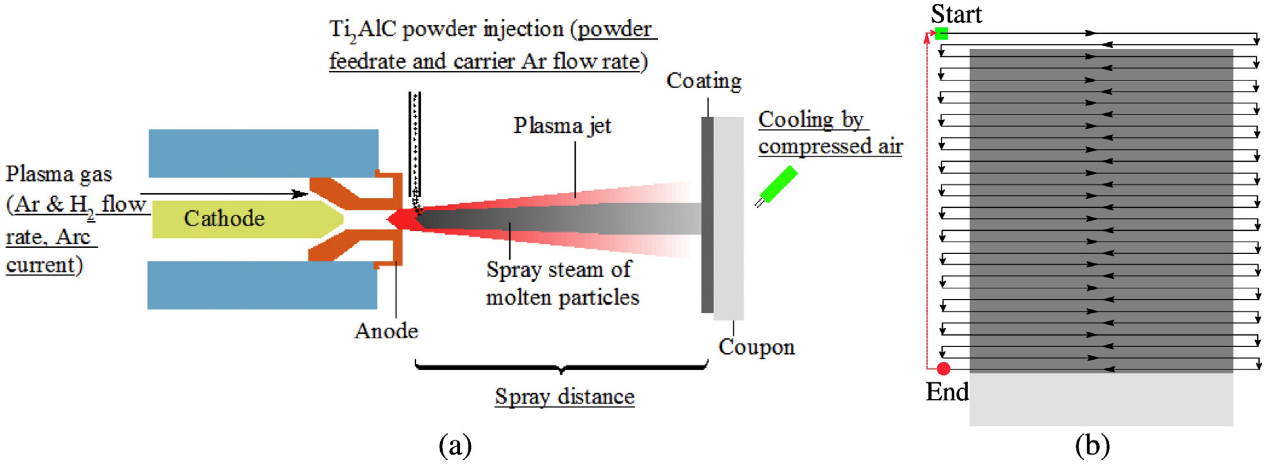

Fig. 1. Illustrations of (a) process parameters which have been systematically tuned (underlined) during the plasma spray of Ti_2AlC powders and (b) the movement path of the spray gun from start (green square) to the end (red circle) in one pass of spray. The light and dark grey regions represent substrate and coating, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)