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C.J. Huang, K. Yang, N. Li, W.Y. Li, M.P. Planche, et al.. Microstructures and wear-corrosion performance of vacuum plasma sprayed and cold gas dynamic sprayed Muntz alloy coatings. Surface and Coatings Technology, 2019, 371, pp.172 - 184. 10.1016/j.surfcoat.2018.09.058. hal-03485872

# HAL Id: hal-03485872 https://hal.science/hal-03485872

Submitted on 20 Dec 2021

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1	Microstructures and wear-corrosion performance of vacuum plasma sprayed and cold gas dynamic
2	sprayed Muntz alloy coatings
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8	
9	Abstract:
10	As one of the important Cu alloys, brass has been implanted in many fields of architecture or fabrication
11	industry. Muntz (Cu60Zn40) brass alloy was used to manufacture the brass coatings in this study due to
12	showing the best corrosion resistance. Two different spray methods i.e. vacuum plasma spray (VPS) and cold
13	gas dynamic spray (CGDS), were chosen to perform the synthesis of brass coatings aiming to avoid oxidation.
14	Upon utilization of VPS and CGDS techniques, spray process is crucial to the microstructures, phase
15	transformation, mechanical property, and wear and corrosion properties of Muntz alloy coatings. Here results
16	show that no oxidation was characterized in both two processes. Nevertheless, a vaporization of 19.32 wt. %
17	Zn occurred during VPS, which would lead to the significant differences in grain size, misorientation
18	distribution, texture and phase composition of VPSed coating from those of CGDSed coating. The CGDSed
19	coating exhibited excellent performances due to a preservation of chemical composition of original feedstock.
20	For example, it yielded a hardness value of $211.8 \pm 9.8$ HV <sub>0.3</sub> , which was nearly two times higher than that of
21	VPSed coating (119.3 $\pm$ 11.6 HV <sub>0.3</sub> ). It was also shown that a significant wear rate reduction ((1.3 $\pm$
22	0.018)×10 <sup>-5</sup> v.s. (2.36 ± 0.39)×10 <sup>-4</sup> mm <sup>3</sup> /mN) and a corrosion resistance enhancement.
23	
24	Keywords: Vacuum plasma spray; Cold gas dynamic spray; Muntz alloy; Microstructure; Wear; Corrosion.

Abbreviations and symbols								
Abbreviation								
PS	Plasma spray	EDS	energy-dispersive X-ray spectroscopy					
APS	Atmospheric plasma spray	SEM	Scanning electron microscope					
VPS	Vacuum plasma spray	OM	Optical microscope					
AS	Arc spray	EBSD	Electron backscatter diffraction					
CGDS	Cold gas dynamic spray	XRD	X-ray diffraction					
HVOF	High-velocity oxygen fuel	TBs	Twinned boundaries					
EIS	Electrochemical impedance spectroscopy	OCP	Open circuit potential					
GB	Grain boundary	HAGBs	High-angle grain boundaries					
LAGBs	Low-angle grain boundaries	CSL	Coincidence site lattice					
Symbol								
r	Radius of worn track, mm	$E_{corr}$	Corrosion potentials, V					
S	Cross-sectional area, mm	i <sub>corr</sub>	Corrosion current density, $\mu A \ cm^{-2}$					
p	Load, N	l	Sliding distance, <i>m</i>					
$\beta_a$	Anodic Tafel slope, $V dec^{-1}$	$\beta_c$	Cathodic Tafel slope, $V dec^{-1}$					



#### 27 1 Introduction

28 Thermal spray, a group of coating processes in which metallic and non-metallic materials deposited in a 29 molten or semi-molten condition to form a coating, is divided into several processes according to the thermal 30 energy source and the kinetic energy of the sprayed materials, such as electric arc spray (AS), plasma spray 31 (PS), and high velocity oxy-fuel (HVOF) spray. Among these processes, PS is mainly divided into 32 atmospheric plasma spray (APS) and vacuum plasma spray (VPS) according to an operating pressure range 33 [1]. During APS, a coating is formed in an open-air environment. Therefore, the metallic coating is easily 34 oxidized and its density will be decreased due to a number of pores [1,2]. With respect to VPS, it can prevent 35 a coating from the oxidation and improves the coating density, since molten droplets will undergo a low 36 atmospheric pressure and a high velocity. Consequently, this kind of Cu coating prepared via VPS generally 37 exhibits the better mechanical properties compared to other thermal spraying processes [3,4] as shown in Fig. 38 1, due to a typical lamellar and dense microstructure, a low porosity and a limited oxygen content.

Acting as a new member of the thermal spray technique, cold gas dynamic spray (CGDS), based on supersonic fluid dynamics and high-speed impact dynamics, is a relatively new solid-state coating process [5-10]. During CGDS, the sprayed powder particles (commonly in a size range of 5-50 µm) are accelerated to a higher velocity changing from 300 to 1200 m/s in a high-speed gas jet, and projected onto a substrate or a previously deposited layer in a nominally solid state (i.e. at a temperature well below the melting point of the 44 powder). CGDS features a higher particle velocity and a lower processing temperature, showing many 45 advantages compared to these conventional thermal spray techniques [9]. For example, the heating effects on 46 both substrates and sprayed powders are rarely observed, since the coating deposition will not allow an 47 explosion of the substrates or sprayed materials to a very high temperature, which will make it possible to 48 deposit this kind of the temperature-sensitive materials without any significant changes in the microstructure 49 of feedstock [5]. In addition, the resulting residual stresses are typically low and mostly compressive 50 compared to thermal spraying, which permits a deposition of relatively thick coatings.

51 The Cu-based alloys, as one of the most versatile engineering materials with numerous excellent properties, 52 such as high strength, good heat conductivity, good corrosion and biofouling resistance, good machinability 53 and ductility [5], have been widely applied within the industrial and electronic fields [6]. Therefore, based on 54 this aim of well developing these coatings, many comparative investigations on preparing Cu and its alloys 55 coatings between conventional thermal spray and cold gas dynamic spray have been disclosed. For example, 56 in Gärtner and Stoltenhoff's studies [3,7], the sprayed Cu particles were completely molten during the arc 57 spray or at least partially molten during the high-velocity oxygen fuel (HVOF) spray. While the CGDSed Cu 58 coating showed a denser microstructure without melting and oxidation, which might suggest that a deposition 59 of Cu using CGDS showed a prominent advantage over these conventional thermal spray processes. Similarly, 60 Li et al. [10] also used VPS and CGDS to obtain the dense Cu-4Cr-2Nb coatings, and almost no oxidation 61 occurred for both depositions. Furthermore, Gassot et al. [4] compared the process of VPS with APS and 62 HVOF and studied the influences of these processes on the microstructures and properties of Cu coatings, 63 indicating that VPSed coating showed a recrystallized structure with the least oxygen content and this was 64 very different from the typical splat structures of APS and HVOF coatings [3,4].

As one of the best-known Cu alloys, bronze has been used as the anti-corrosion and anti-friction coating materials, such as bearings and lubricant materials. A fabrication of bronze alloy coatings and their composite coatings have been obtained by electro deposition [11], thermal spray [12,13] and cold gas dynamic spray [13-15]. For instance, the microstructures and wear performances of bronze-based coatings deposited by APS and CGDS have been investigated by Miguel et al. [13], and showing that the CGDSed bronze coatings exhibited a higher sliding wear resistance due to a better cohesion, a higher matrix hardness and better distribution offine alumina.

72 On the other hand, the brass alloys showing excellent properties (lightness, mechanical strength, corrosion 73 resistance, etc), have extended to numerous applications, such as architectures, industrial fabrication, maritime, 74 etc. [16]. However, the brass coatings were mainly prepared by electro-deposition [17,18]. The studies on 75 preparing the brass coatings was given a very small number of attempts to manufacture them with thermal 76 spray processes [19], which will seriously limit its numerous applications in many fields. Muntz brass allow 77 with a two-phase  $(\alpha+\beta)$  structure, patented in 1832 by George F. Muntz [20], has showed many interesting 78 properties [21]. Owing to maintaining an anti-corrosion property with a lower cost, Muntz alloy has recently 79 became the main material for boat sheathing and propeller, which work under a marine environment. Thus, 80 the thermal sprayed methods featuring of high deposition rate and rapid manufacturing are essential to 81 facilitate the application of brass coatings. Thus, herein, we selected the Muntz alloy powder for preparing the 82 non-oxidized and dense brass coatings using the vacuum plasma deposition process, compared with the solid-83 state process of cold spray [22]. The effects of spray processes (VPS and CGDS) on the microstructures, the 84 phases and the wear and corrosion resistances of the Muntz alloy coatings were compared and explored.

#### 85 **2. Experimental procedure**

### 86 **2.1 Powder**

Fig. 2 shows the surface and cross-sectional morphologies of the gas-atomized Muntz alloy powder (ECKA Granules Metal Powders Ltd., UK). An irregular shape is obviously shown in Fig. 2. The SEM cross-sectional morphology of a single non-etched Cu60Zn40 particle appears free of porosity (Fig. 2c). An average grain size of 2.1 µm was estimated upon etching (Fig. 2d). The chemical composition of Cu60Zn40 alloy powder was detailed in Table 1.

A size distribution of used Muntz powder was measured with a Mastersizer 2000 laser particle size distribution, showing a Gaussian size distribution ranging from +15.1 to -69.7  $\mu$ m with an average diameter of 35.6  $\mu$ m (Fig. 3). The powder was used to be directly deposited without an optimization of powder morphology.

### 96 2.2 Coating deposition

97 VPS was carried out using a Metco A-2000 VPS equipment (Sulzer Metco F4-VB plasma torch, 98 Switzerland) under a low-pressure condition. The working gases were argon and hydrogen with an arc current 99 of 720 A and an electrical plasma power of 43 kW. The substrate surface temperature was measured to be 100 about 800 °C by a monochromatic pyrometer (Land Infrared type M2). The standoff distance from the nozzle 101 exit to the substrate surface was 250 mm. The coating was deposited on E355 steel plates, which were sand-102 blasted with the SiO<sub>2</sub> powder under ambient condition. Optimized processing parameters of VPS are 103 summarized in Table 2.

104 CGDS was carried out using a commercial Kinetic 3000 system (CGT GmbH, Germany). This 105 installation consists of a control cabinet, a gas heater, a powder feeder and a spray gun equipped with different nozzles (Laval nozzle) depending on the nature of the material to be sprayed. The nozzle (MOC-24, CGT) 106 107 having a cylindrical section was used in this study. The brass coatings were deposited on the Cu alloy plates, 108 which were sand-blasted with the SiO<sub>2</sub> powder under the ambient condition. To achieve the optimal 109 processing parameters and best quality of Muntz coatings, various parameters were tested for CGDS process. 110 Gas temperature were changed from 250 °C to 550 °C and gas pressure was fixed at 2.8 MPa. The selecting 111 principle is based on maximum density and low manufacturing cost. The relative density of CGDS Muntz 112 coating was measured by an analytical balance based on Archimedes principle. Detailed optimized parameters 113 of CGDS process used in this work are provided in Table 3.

#### 114 **2.3 Characterizations**

115 The morphologies of powder and the microstructural and phase characterizations of the coatings were 116 measured by an optical microscope (OM, Nikon, Japan) and scanning electron microscope (SEM, 117 JSM5800LV, JEOL, Japan) equipped with an electron backscatter diffraction (EBSD) system. The phase 118 composition of sprayed coatings was characterized by X-ray diffraction (XRD). The chemical composition of 119 the powder and the coatings was quantified using the SEM equipped with energy-dispersive X-ray 120 spectroscopy (EDS, Oxford Instruments INCA system, UK). The coating microhardness was tested by a 121 Vickers hardness (Leitz, Germany) indenter with a load of 3 N for 15 s, and more than 20 values were 122 randomly tested and averaged to evaluate the coating hardness.

123 Friction tests were performed on a ball-on-disk CSM tribometer under an ambient condition (temperature: 124 19 °C, humidity: 53 %). Before friction tests, all deposit surfaces were polished to a roughness (Ra) of about 125 0.2 µm. The counterpart was a 6 mm diameter 100Cr6 steel ball with a mirror finished surface. The friction 126 force was measured with a sensor and dynamically recorded into a computer. The friction coefficient was 127 computed when the friction force was divided by the applied load. The applied load and sliding velocity were 128 5 N and 0.1 m/s, respectively. The diameter of the worn track and the sliding distance were 6 mm and 30 m, 129 respectively. The wear rate defined as the worn volume per unit of normal load and sliding distance was 130 calculated using the equation below:

131 
$$v_r = \frac{2\pi rS}{p \times l}$$

where r (mm) is the radius of worn track. S (mm<sup>2</sup>) is the cross-sectional area of the track circle. p (N) is the load, and l (m) is the sliding distance. After the completion of 30 m sliding distance, the cross-sectional area of the worn track was measured using an Altisurf 500 profilometer with the given average values corresponding to a set of 5 random positions along the worn track for each sample.

136 All electrochemical measurements were carried out using a standard three-electrode that are exposed to 137 an electrolyte of a non-deaerated and unstirred 3.5 wt. % NaCl aqueous solution at ambient temperature. Prior 138 to the electrochemical testing, all coatings removed from the substrates were ground with abrasive papers up 139 to 2000 grit, and finally rinsed in an ultrasonic bath with acetone. The coating was used as the working 140 electrode immersed in the solution, and a platinum foil and a saturated calomel electrode served as the counter 141 electrode and reference electrode, respectively. The open circuit potential (OCP) was first recorded in a three-142 electrode cell and a steady state OCP was reached after immersing in the test solution for 1.5 hours. And then 143 Tafel polarization curves were plotted by starting scanning electrode potential from -0.25 V to +0.25 V versus 144 OCP at a scanning rate of 0.167 mV/s. Electrochemical impedance spectroscopy (EIS) was performed with a 145 voltage amplitude of  $\pm 5$  mV in the frequency ranging from 0.01 to 100 kHz. Corrosion current densities (*i<sub>corr</sub>*) 146 were estimated from the Tafel extrapolation of the cathodic and anodic slopes using Power Suite software. 147 EIS measurements were repeated three times in order to insure fare discussions and the ZView software was 148 used for the fitting of the resulted spectra..

#### 149 **3. Results and discussion**

#### 150 **3.1 Element composition**

151 Elemental mapping of the original powder analyzed by EDS (red colour representing Cu, green color 152 representing Zn) shows a considerable amount of 59.45 wt.% Cu (Fig. 4a), which is consitent with the 153 comercially technical data (58.5-61.5 wt. %). After ungergoing a high-temperature and low-pressure 154 deposition process of VPS, the composition proportion of Cu element increased because of a significant loss 155 of 19.32 wt. % Zn under the present experiment condition. Generally, Zn element has the relatively lower 156 melting point (419.5 °C) and boiling point (907 °C). Therefore, a vaporization of Zn is very easily occurred. 157 This phenomenon is similar to the physical vacuum dealloying process, which is commenly used to fabricate 158 the three-dimensional porous metals [23]. However, a dense structure was formed in the VPSed coating as 159 shown in Fig. 4b. When observed the Fig. 4c, the Cu element composition shows a similar result to that of the 160 original powder, which is attributed to the fact that the deposition of CGDS takes place through the intensive 161 plastic deformation of particles upon impact in a solid state at a temperature well below the melting point of 162 spray material. Consequently, the deleterious effects of oxidation, decomposition, and melting inherent in the 163 thermal spraying could be eliminated [24].

#### 164 **3.2 Coating microstructures**

165 The typical cross-sectional microstructures of Muntz alloy coatings via VPS and CGDS are shown in Fig. 5. 166 A homogeneous appearance and a dense microstructure (porosity: 0.35 %) are observed in the VPSed coating 167 (Fig. 5a). This microstructure is composed of molten and semi-molten particles, which is similar to the 168 lamellar structure [4]. Additionally, a recrystallized structure has been produced due to the high temperature 169 during VPS, which suggests that the metallurgical bonding is main bonding mechanism as shown in Fig. 5b. 170 As indicated by Gassot et al. [4], a recrystallized structure was presented in the VPSed coating with very low 171 oxygen content, which was different from those of the deposited coatings by APS and HVOF. As for the 172 VPSed coating, the molten and semi-molten particles have experienced a coupled effect of zinc vaporization 173 and rapid solidification under the high impact velocity. The remaining Zn was dissolved in the Cu, and 174 forming a substitutional solid solution of Zn in Cu. As also known, a formation of the substitutional solid 175 solutions between Cu and Zn is governed by the Hume-Rothery rules. The solubility of a metal with higher

valence in a solvent lower valence is more compared to the reverse situation (i.e. Zn is much more soluble in
Cu). Furthermore, the low stacking fault energy of Cu-Zn alloys contributes to forming the fine twins in the
solid solution, as distinguished inside the particles presented by the inset in Fig. 5b.

179 As for the CGDSed coating, the Muntz particles are deformed and elongated, and the distorted particles are 180 bonded to the adjacent ones (Fig. 5c). A presence of interface between these interlocked particles is noticeable, 181 which is taken into account the mechanical bonding mechanism in the CGDSed coating [7]. However, when 182 compared to the microstructure of the pure copper coatings [7,10], the deformability of Cu-Zn particles is not 183 sufficient to fill in all the gaps between the deposited particles owing to the relatively higher hardness, which 184 leads to a presence of pores and non-bonded interfaces in CGDSed coating (porosity: 1.12 %). When observed 185 in the etched state (Fig. 5d), the impact-induced deformation twins are clearly shown in the interior particle as 186 marked by the arrow.

187 EBSD investigations were performed for studying the detailed microstructures of the VPSed and CGDSed 188 coatings. EBSD reconstructed orientation maps and grain size distribution of these two coatings are shown in 189 Fig. 6. The VPSed coating shows a recrystallized structure of fine grains with an average grain size of 0.35 190 µm (Fig. 6a), which is due to the presence of high temperature in VPSed coating inducing a uniform 191 interdiffusion and recrystallization. Therefore, the oxide layers are not observed, thus forming a uniform 192 coating. By contrast, the CGDSed coating exhibits a flattened structure with an average grain size of 1.9 µm 193 (Fig. 6b). Some Cu60Zn40 particles are extremely elongated and distorted into the long strips while others 194 remains undistorted, suggesting an heterogeneous plastic deformation during the deposition process. 195 Furthermore, it is clearly that the high-velocity impact effect results in a fact that grains near the interface are 196 smaller than those in the interior due to the dynamic recrystallization [24,25]. Thus, the grains near the 197 particle boundaries are oriented, which are surround by the interior of deposited particle. Moreover, certain 198 defects (e.g., relatively large pores) are also observed due to an insufficient deformation in the sprayed coating 199 process, which will result in a poor bonding structure.

We applied the detailed pole figures for twinned microstructure characterizations (see white circle in Fig. 6a). In the <110> pole figure, clusters of purple and pink spots correspond to the fine grains in EBSD map are clearly seen. Three <110> directions (both purple and pink) located on the coherent (111) twin plane (a red arc) are shared by the twinned and untwined regions. This twinned nature can also be evidenced in <111>pole figure, where the direction circled is a common <111> direction to both purple and pink grain. The (111)twin plane corresponding to this common <111> direction, is also indicated by a red arc in this pole figure.Clearly, those three pairs of non-common directions have a symmetric relation with respect to the twin plane.

207 The grain boundary (GB) map of the VPSed coating and the misorientation angles distribution are shown in 208 Figs. 7a and 7b, respectively. As can be seen, a recrystallization is resulted from the high temperature of the 209 plasma jet and the rapid solidification during VPS, which is responsible for the generation of these fine grains. 210 Considering all GBs misorientation angles that are bigger than are 2°, the VPSed coating shows a large 211 number of high-angle grain boundaries (HAGBs) at a fraction of 84.36 % and a small quantity of low-angle 212 grain boundaries (LAGBs) at a fraction of 15.64 %. The LAGBs are accumulated in the certain regions, while 213 other regions show a more uniform and larger grain distribution in the VPSed coating. This phnomenen could 214 be ascribled to a high substrate temperature produced by the long plasma jet, causing a self-annealing of the 215 deposited particles. Indeed, this self-annealing is beneficial, because it provides stress relief and 216 recrystallization, resulting in an enhanced interparticle bonding [26]. Therefore, these regions with less 217 LAGBs accumulation and larger grain formation could be induced by the self-annealing effect. On the other 218 hand, a fraction of 71 % of HAGBs (red lines in Fig. 7a) are responsible for the Coincidence Site Lattice (CSL) 219  $\Sigma$ 3 boundaries due to the recrystallization in the VSP process, because massive annealing twins occurred 220 around 60 ° after VPS (Fig. 7b).

The GB map of the CGDSed coating is shown in Fig. 7c, and the corresponding distribution of misorientation angles is shown in Fig. 7d. The CSed coating is characterized by HAGBs at a fraction of 22.6 %, and LAGBs remaining at a fraction of 78.4 %, because a high density of dislocations and sub-grains are presented in the extensively deformed particles after impact. When a particle with a sufficient highvelocity impact upon the substrate or on previously deposited particles [21], a large number of dislocations accumulate near the grain boundaries, which might be responsible for the HAGBs in these intensively elongated grains [27,28].

#### 228 3.3 Microtextures

The microstructure evolutions induced by the plastic deformation during the impact is closely related to the changes in the texture. Thus, the texture distribution in the coatings fabricated by VPS and CGDS need to be well investigated. A comparison of the orientation data obtained for the VPSed and CGDSed coatings is presented in Fig. 8, in the form of <100>, <110> and <111> pole figures. It is found that VPSed coating shows a homogeneous texture, suggesting that the preferred orientation is reduced or even eliminated due to the coupled effects of recovery of stress relief and recrystallization during VPS [26]. However, the CGDSed coating shows a little stronger crystallographich texture after an intensively plastic deformation.

#### 236 **3.4 Phase transformation**

237 The structural and compositional analysis of the Muntz powder, and the VPSed and CGDSed coatings were 238 carried out by the XRD patterns as shown in Fig. 9. Original powder is consisted of  $\beta'$  phase due to the rapid 239 solidification in the gas atomization. However, only  $\alpha$  diffraction peak is detected after VPS, and this is due to 240 the vaporization of Zn element and the formation of  $\alpha$  solid solution. Compared to the CGDSed coating, it is 241 consisted of two main phases, i.e.  $\alpha$  and  $\beta'$ , which is very different from that of the powder and the VPSed 242 coating, thus implying that CGDS induces structural changes and phase transformations. Because a severe 243 plastic deformation at high strain rate combined with high pressures are up to more than 10 GPa, and are 244 extremely high cooling rates [28]. Furthermore, the peak widths of the CGDSed coating are also broadened, 245 which is perhaps caused by the formation of sub-grains and micro-strain (see Fig. 7c). As for the VPSed 246 coating, the increased peak intensity indicates a higher crystallite size. Furthermore, the increased twins in the 247  $\alpha$  grains (see Fig. 7a) will lead to a right shift of  $\alpha$ -phased peaks.

For a further identification in the phase evolution, the EBSD phase maps were used to characterize the phase transformation. The twin distribution and the phase map are shown in Figs. 10a and 10c. The twins are represented by the yellow lines, and the red, bule and yellow regions are respective to the  $\alpha$ ,  $\gamma$  and  $\beta'$  phases. The annealing twins are uniformly presented with only  $\alpha$  phase after VSP as shown in Fig. 10a. Furthermore, a little non-equilibrium phase of  $\gamma$ -Cu<sub>5</sub>Zn<sub>8</sub> (blue color) with a complex cubic structure is presented in these regions of a higher concentration of Zn due to the thermo-mechanical effect. However, compared to the CGDSed coating, two solid solutions in the coating, i.e. the majority of  $\alpha$  and a little  $\beta'$  intermetallic phase, are 255 shown in the Fig. 10c. In the  $\alpha$ -phase, the presence of twins in the CGDSed coating is marked by the black 256 arrow, which is attributed to the highly impact induced deformation.

#### 257 3.5 Microhardness

A typical Vicker indentation for the VPSed and CGDSed coatings under the force of 3 N are characterized by the regular shape as illustrated in the Fig. 11. In addition, the VPSed coating shows a noticeable increment in the indentation size compared to that of the CGDSed coating, which implies that the VPSed coating has a lower resistance to the compressive load. In Li's previous study, it was indicated that some cracks were formed during the indentation process, which might be due to the weak particle interfaces [29]. However, it is not the same case in the present work, which suggests a good resistance in both coatings.

264 A comparison of the microhardness value for the VPSed and CGDSed coatings with a corresponding EDS 265 analysis for the indentations are shown in Fig. 12. The microhardness measurements on the CGDSed coating 266 yields the value of  $211.8 \pm 9.8$  HV<sub>0.3</sub>, which is nearly two times higher than that of the VPSed coating (119.3) 267  $\pm$  11.6 HV<sub>0.3</sub>). In addition, the hardness value of the CGDSed coating is much higher than the bronze coating 268 of CuSn8, and comparable to that of the TiN/CuSn8 composite coating fabricated by cold spray [30]. The 269 significantly higher hardness in CGDSed coating is due to the strain-hardening effect during the particle 270 impact [31]. On the other hand, the solid solutions depending on the proportion of Zn element may also have 271 an effect on the microhardness [32]. In addition, the lower hardness of the VPSed coating is ascribed to the 272 stress relief and the disapperance of  $\beta'$  intermetallic phase during the self-annealing and Zn vaporization 273 process.

#### 274 **3.6 Wear behavior**

#### 275 **3.6.1 Friction coefficient and wear rate**

The COF evolution for the VPSed and CGDSed coatings with the sliding time during the dry sliding wear contact test is shown in Fig. 13a. After a very short run-in period, both COFs arrives at a relatively steady state. The COF of the VPSed coating shows a much higher value than that of the CGDSed coating. For VPSed coating, the COF is approximately between 0.57 and 0.9. While in the case of the CGDSed coating, it shows a quite stable and low value of 0.19. The higher COF of the VPSed coating is produced due to the lower microhardness compared to that of the CGDSed coating [33]. Fig. 13b illustrates the wear rates of the two coatings. As can be seen that the CGDSed coating shows a reduced wear rate ( $(1.3 \pm 0.02) \times 10^{-5} \text{ mm}^3/\text{mN}$ ) by more than one order of magnitude compared to that of the VPSed coating ( $(2.36 \pm 0.39) \times 10^{-4} \text{ mm}^3/\text{mN}$ ). This suggests a higher wear resistance of the CGDSed coating, and it is also correlated well with the higher microhardness of the CGDSed coating [34]. The significant discrepancies in the increasing the COF and the decreasing the wear rate of CGDS coating are related to the tribological mechanism.

### 287 3.6.2 Wear mechanism

288 Fig. 14a shows an overview of worn track of the VPSed coating. The distribution of the Cu, Zn, O and Fe 289 elements across this worn track is obtained from the result of EDS line profilng (Fig. 14b). The scan position 290 is indicated using a vellow line in Fig. 14a. The EDS line profilng indicates that no occurrence of oxdication 291 was occurred during the friction test. Cu and Zn elements are homogeneously distributed within the track. In 292 addition, some brim-liked shapes are observed on the worn surface of VPSed coating, which are closely 293 related to the stick-slip motion feature of the sliding ball. When repeated under the shear forces, the cracks 294 would be produced at this interface in the direction perpendicular to the sliding direction and finally, material 295 can be detached from the coating. In such a case, the adhesion, between the deposit and the sliding ball, is a 296 dominant factor for the tribological behavior. Those brim-liked shapes are assumed to be formed by the 297 superior deformation of the deposit surface parallel to the sliding direction. Indeed, this phenomenen occurs 298 under the combined conditions of large adhesion force between the sliding pair and low hardness but high 299 ductibility of the VPSed coating.

However, the worn surfaces and the elements distribution of the CGDSed coating indicate a different tribological mechanism. There is no obvious evidence of delamination on the worn surface of the CGDSed coating. The wear behavior of the CGDSed coating is featured of micro-abrasive and micro-plowing proved by the worn surface. The CGDSed coating shows a strain-hardened microstructure with the hard and brittle phase of  $\beta$ ', resulting in decreasing the plasticity and reducing the adhesive wear. Hence, the worn surface of the CGDSed coating presents a relatively smooth morphology after the friction test.

#### **306 3.7 Electrochemical behavior**

Tafel polarization and EIS diagrams were utilized to explore the corrosion behaviors of the VPSed and CGDSed coatings in 3.5 wt. % NaCl solution. Fig. 15 shows the Tafel polarization curves of the VPSed and CGDSed coatings. The Tafel curve parameters, e.g. corrosion potentials ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), anodic Tafel slope ( $\beta_a$ ) and cathodic Tafel slope ( $\beta_c$ ) were extracted using Tafel's extrapolation; the results are present in Table 4.

312 The spray process has a significant influence on the polarization characteristic of the obtained coatings. The 313 VPSed coating shows a higher  $E_{corr}$  value (-0.218 V) than that of CGDSed coating (-0.345 V) due to an excessive 314 loss of Zn (the standard electrode potentials:  $E_{Zi}$  = - 0.763 V and  $E_{Cu}$  = + 0.337 V). Generally, more positive  $E_{corr}$ 315 reflects the higher degree of thermodynamically corrosion resistance of materials [35]. In addition, the cathodic 316 Tafel slopes ( $\beta_c$ ) of both coatings are higher than anodic Tafel slopes ( $\beta_a$ ), suggesting that they are dominated by 317 the cathode reaction [36]. Furthermore, the current density used to assess the kinetics of corrosion reactions, is essentially proportional to the corrosion rate. The  $i_{corr}$  values of the VPSed coating ( $i_{corr}$  = 0.783  $\mu$ A/cm<sup>2</sup>) coating is 318 319 higher than that of the CGDSed coating ( $i_{corr} = 0.235 \,\mu\text{A/cm}^2$ ), indicating that a lower corrosion rate and a higher 320 corrosion resistance in CGDSed coating than that of the VPSed coating. In fact, electrochemical process of 321 galvanic coupling plays a more significant effect on the dezincification corrosion in the VPSed coating, because 322 the lower fraction of Zn (20.54 %). In addition, the phenomenon of passivation occurs due to the film formation 323 on the VPSed coating surface.

324 To further investigate the corrosion performances of the two brass coatings by different spray methods, AC 325 impedance spectroscopy was also monitored. EIS analysis are presented as both Nyquist (Fig. 16a) and Bode 326 (Fig. 16b) plots of the VPSed and CGDSed coatings obtained experimentally at their corresponding OCPs. As 327 for the VPSed coating, the Nyquist plot consists of a single semicircle correlating to the charge transfer 328 process at higher frequencies and a Warburg line correlating to the diffusion of reactants toward or away from 329 the surface at lower frequencies. This suggests the corrosion mechanism of the VPSed coating is controlled by 330 both the charge transfer and the diffusion process. In addition, the diameters of semicircles of the CGDSed 331 coating is larger than that of the VPSed coating, which implies that the CGDSed coating shows the higher 332 charge transfer resistance and thus the better corrosion resistance. Thus CGDSed coating has much higher impedance value than that of the VPSed coating as indicated by the Bode plot in the Fig. 16b. The Nyquistand Bode plots are quite well in agreement with the polarization behaviors.

#### 335 4 Conclusions

336 In this study, a vacuum deposition process as VPS and a solid-state deposition process as CGDS, were 337 chosen for depositing Muntz alloy coatings to avoid oxidation. Microstructures and key properties of coatings 338 are comparatively studied, and main conclusions are that: A significant vaporization of 19.32 wt. % Zn 339 occurred during VPS, while CGDSed coating showed a similar element composition to that of the original 340 powder. The VPSed coating (porosity: 0.35 %) shows a dense and a recrystallized microstructure with an 341 average grain size of 0.35 µm. While the CGDSed coating (porosity: 1.12 %) exhibits a flattened structure 342 (average grain size of 1.9 µm) with the presence of pores and non-bonded interfaces The VPSed coating has a 343 large number of HAGBs at 84.36 % (71 % of HAGBs are CSL Σ3 boundaries) and a few LAGBs at 15.64 %. 344 The CGDSed coating is characterized by HAGBs at 22.6% and LAGBs in the remaining 78.4 %, showing a 345 high density of dislocations and sub-grains in the deformed grains. The VPSed coating exihibites a 346 homogeneous texture, indicating that the preferred orientation is reduced or even eliminated due to the self-347 annealing effect during VPS. However, the CGDSed coating shows similar crystallographich texture after an 348 intensively plastic deformation. Only  $\alpha$  diffraction peak was detected after VPS due to the vaporization of zinc 349 and formation of  $\alpha$  solid solution. However, the CGDSed coating is consisted of  $\alpha$  and  $\beta$ ' because of the severe 350 plastic deformation at high strain rate. The microhardness of the CGDSed coating yields the value of  $211.8 \pm$ 351 9.8 HV<sub>0.3</sub>, which was two times higher than that of the VPSed coating (119.3  $\pm$  11.6 HV<sub>0.3</sub>). While in the case 352 of CGDSed coating (( $1.3 \pm 0.02$ )×10<sup>-5</sup> mm<sup>3</sup>/mN), it shows a reduced wear rate by more than one order of 353 magnitude compared to that of the VPSed coating ( $(2.36 \pm 0.39) \times 10^{-4} \text{ mm}^3/\text{mN}$ ). The galvanic corrosion 354 significantly affects the dezincification corrosion in the VPSed coating owing to its higher fraction of copper, 355 which is in agreement with the higher impedance of CGDSed coating.

#### 356 Acknowledgements

The C.J. Huang author would like thank the support from the program of CSC (201404490058). The W.Y. Li author would like thank the support from the program of the National Natural Science Foundation of China (51574196) and the 111 Project (B08040).

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## **Tables**

Table 1. Chemical composition of Muntz brass alloy powder (wt. %).

Elements	Cu	Fe	Pb	Sn	Zn
Composition	58.5 - 61.5	≤0.15	0.25 - 0.7	≤ 0.26	bal.

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## Table 2. Optimized parameters of VPS used in this work.

Pressure	Arc current	Arc voltage	Argon gas flow rate	Hydrogen flow rate	Powder gas flow rate	Powder feed rate	Spray distance
100 Pa	720 A	60 V	50 NL/min	5 NL/min	3 NL/min	15 g/min	250 mm

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## Table 3. Optimized parameters of CGDS used in this work.

Pressure	Temperature	Standoff distance	Hatch distance	Nozzle moving speed	Propulsive gas
2.8 MPa	450 °C	30 mm	5 mm	20 mm/s	Compressed air

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## Table 4. Electrochemical parameters obtained from Tafel polarization curves

## of VPSed and CGDSed coatings.

Process	$E_{corr}(V_{SCE})/V$	$i_{corr}/(\mu A \cdot cm^{-2})$	$\beta_c/(V \cdot dec^{-1})$	$\beta_a/(V \cdot dec^{-1})$
VPS	- 0.218	0.783	0.065	0.039
CS	- 0.345	0.235	0.141	0.052

#### 421 Figures



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Fig. 1. Mechanical resistance and elongation of Cu coatings by thermal spraying [3,4].



426 Fig. 2. SEM micrographs of (a) the used Muntz alloy powder and (b) high magnification of a particle, (c) non-427 etched and (d) etched cross-section of a single particle.



Fig. 3 The size distribution of the used Muntz powder.



431 Fig. 4. EDS maps and element compositions of (a) Muntz powder, (b) VPSed and (c) CGDSed coatings.

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Fig. 5. SEM micrographs of (a and b) VPSed and (c and d) CGDSed Cu60Zn40 coatings.



439 Fig. 6. EDSD maps for (a) VPSed and (b) CGDSed coatings, (c) grain size distribution of these two coatings, and (d) pole figures obtained from the white circle in (a), the common, <110> and <111> directions are 440 441 marked with small circles. The red circular arcs represent the (111) twin planes.



444 Fig. 7. Grain boundary maps of (a) VPSed and (c) CSed coatings, the black, blue and red lines in EBSD maps
445 corresponding to the HAGBs (θ≥ 15°), LAGBs (15° > θ >2°), and (twinned boudaries) TBs, respectively.
446 Misorientation angle distribution of (b) VPSed and (d) CGDSed coatings.



Fig. 8. Pole figures of (a) VPSed and (b) CGDSed coatings.





Fig. 9. XRD patterns of Muntz alloy powder, VPSed and CGDSed coatings.



455 Fig. 10. Phase maps of (a) VPSed and (c) CGDSed coatings [22], and their phase proportions (b) and (d). 456 The yellow lines in (a) and (c) in EBSD maps corresponding to the TBs, and the red, bule and yellow regions 457 with respective to the  $\alpha$ ,  $\gamma$  and  $\beta'$  phases.





Fig. 11. Cross-sectional SEM micrographs of VPSed and CGDSed coatings after indentation.

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464 Fig. 13. Variation of COFs (a) and wear rate (b) of VPSed and CGDSed coatings with sliding time

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of 10 min at room temperature.





Fig. 15. Tafel polarization curves of (a) VPSed and (b) CGDSed coatings.









Fig. 16. Nyquist (a) and Bode (b) plots of the VPSed and CGDSed coatings.