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HVOF sprayed Al–Cu–Cr quasicrystalline coatings from coarse feedstock powders



Yingqing Fu*, Tianxiang Peng, Deming Yang, Chengqi Sun, Yuzhen Chen, Yang Gao

Department of Materials Science and Engineering, Dalian Maritime University, Dalian 116026, China

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ABSTRACT

Al-Cu-Cr quasicrystalline (QC) coatings were prepared from coarse feedstock powders by a high velocity oxyfuel (HVOF) system DJ2700. The contrast experiments were performed by low power atmospheric plasma spray (LPAPS) using the same Al₆₅Cu₂₀Cr₁₅ QC powders, and by HVOF spraying Cu180 powders with the size of 44–61 µm. The phase composition, microstructure and microhardness properties of the QC coatings were investigated. XRD results showed that the feedstock and coatings contained a predominant phase, icosahedral quasicrystal (IQC) I-Al₆₅Cu₂₄Cr₁₁, and three minor crystalline phases: α -Al₆₉Cu₁₈Cr₁₃, θ -Al₁₃Cr₂ (i.e. Al₈₃Cu₄Cr₁₃) and E-Al₂Cu₃. A qualitative analysis on the XRD patterns indicated that, a HVOF-sprayed coating contained more IQC and fewer crystalline phases in the one deposited by LPAPS. Moreover, the higher the input heat energy, the fewer IOC and the more crystalline phase the coating contained, for not only HVOF but also LPAPS. As confirmed by experimental results, when the HVOF-sprayed QC particle impacted onto the substrate surface, the unmelted solid part of particle broke up, and the previously deposited coating portion was deformed and densified and even cracked by impingement of the in-flight particles with high velocity; which minified splats and densified the as-sprayed coating. Thus, the HVOF-sprayed coatings from such coarse (61–74 µm) QC powders had much smaller splats and much denser microstructures with lower porosity and higher microhardness, compared with those deposited by LPAPS using the same feedstock, although the preferential particle size of feedstock powders for HVOF spraying is conventionally 5-45 µm. Furthermore, based on the contrast experimental results, the necessary and sufficient conditions for occurrence of the particle impact breakage behavior in the thermal spray process are: (1) the high brittleness of feedstock and (2) the high velocity and low melting degree of spray particles, respectively.

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1. Introduction

Since being firstly reported in 1984 [1,2], quasicrystalline (QC) materials have become the subject of intense study due to their exceptional structure and properties [3–9]. After 30 years of quasicrystal studies, the focus of research is currently shifting closer to the reality; much interest is nowadays concentrated on finding practical production techniques and applications for these materials. The established technology of aluminum fabrication makes the Al-based QC alloys more attractive than many other quasicrystalline alloys [10]. However, because quasicrystals are brittle in bulk at ambient temperature, most proposed applications employ QC films/coatings [4–6]. Depositing QC coatings onto metallic substrates allows the advantages of QC alloys, such as their surface properties, to be emphasized, while their disadvantages, such as room-temperature brittleness, can be compensated for by the substrate materials.

Various techniques are available for QC coating production, such as magnetron sputtering [11], simultaneous vapor deposition [12], laser

ablation [13], ion-beam mixing [14], ion implantation [15], and thermal spraying [16–21]. Compared with the other techniques, thermal spraying is more versatile in industrialized QC coating production, with a more extensive adaptability; and the coating fabricated by these techniques is more robust [22] and wear-resistant than the one by the others. Moreover, a commercial application of QC coating has emerged, and the product is a cookware surface coating named Cybernox®, deposited by thermal spraying techniques [20].

Thermal spraying techniques are divided, according to the way the energy or heat is provided to melt the material or give it enough plasticity, to allow the formation of the coatings [23]. They usually include flame spraying, high velocity oxy-fuel (HVOF) spraying, detonation spraying, wire arc spraying, plasma spraying and so on. Widely used for many industrial applications, HVOF spraying is probably the best among the thermal spray techniques for some specific needs [24]. It has been well understood that the highest particle velocity can be achieved by spray particles with heat source of the highest velocity; and the highest particle temperature is associated with heat source of the highest temperature [25,26]. Because the maximum temperature of plasma jet reaches over 10,000 K [27], spray particles can be heated to a high temperature by plasma jet with a medium velocity. Although

^{*} Corresponding author. Tel.: +86 411 84723586; fax: +86 411 84729611. *E-mail addresses:* yingqing_fu@aliyun.com, fuyingqing@dlmu.edu.cn (Y. Fu).



Fig. 1. SEM micrographs of $Al_{65}Cu_{20}Cr_{15}$ QC (a) and Cu180 (b) feedstock powders.

HVOF is characterized by high velocity and low flame temperature [27], the flame temperature is significantly influenced by the type of fuel gas and flame conditions. As shown in [28], the HVOF flame temperature using propane as fuel could reach to over 3100 K, and the spray particle velocity in it ranged from 300 to 1200 m/s [29]. HVOF-sprayed coatings are commonly thick and dense with less oxidation [25,26], and typically with reduced changes in phase composition, compared with atmospheric plasma-sprayed ones [30]. Due to the above-mentioned features, HVOF spraying is advantageous for the fabrication of QC coatings, and developing HVOF-sprayed QC coatings for industrial applications may be interesting and valuable.

It can be recognized that the heating and accelerating rates of spray particles increase with decreasing particle size [31]. It has also been found that the oxygen content in HVOF-sprayed alloy coatings increases in an exponential fashion with the decrease of spray particle size, and the oxidation of spray alloy particles becomes remarkably severe when the particle size is smaller than 45 μ m [32]. Thus, in the current study, the Al₆₅Cu₂₀Cr₁₅ QC powders with a size distribution ranged from 61 to 74 μ m, were chosen as feedstock, although the preferential

	-			
High	velocity	oxy-fuel	spray	parameters.

Tabla 1

particle size of feedstock powders for HVOF spraying is conventionally 5–45 µm [26]. Such coarse powders, which reduced the vaporization of aluminum and oxidation of spray particles to facilitate the formation of Al-based QC phases, were HVOF and low power atmospheric plasma [33–37] sprayed respectively. Another finer feedstock, the Cu180 powder with the size of 44–61 µm, was HVOF-sprayed using identical process parameters. Based on the contrast experiments, the breakage behavior of HVOF-sprayed QC particles after impacting onto the AISI 1045 steel substrate was examined. The influences of spray particle impact breakage on the coating microstructure, the necessary and sufficient conditions for its occurrence in the thermal spray process, were clarified respectively in this paper (which is extremely different from the previous paper [36]). Furthermore, no study on the impact breakage of HVOF-sprayed QC particles has been reported.

2. Experimental details

2.1. Spraying materials and process

Scanning electron microscope (SEM) micrographs of the feedstock powders are shown in Fig. 1. The spherical QC powders (Fig. 1a), produced by gas atomization of a liquid melt with a nominal composition of $Al_{65}Cu_{20}Cr_{15}$ [36–38], had the size ranged from 61 to 74 µm. Another water atomized feedstock, Cu180 powders (Fig. 1b) for the contrast experiment with the size of 44–61 µm, had a nominal composition of Cu–5 wt.% Ni–10 wt.% Al. Both the feedstocks were thermally sprayed onto the previously grit-blasted AISI 1045 steel substrates respectively, with an oxygen–propane HVOF torch DJ2700 (Diamond Jet 2700hybrid, Sulzer Metco, Westbury, NY, USA), and the HVOF spray parameters are presented in Table 1. The low power atmospheric plasma spray (LPAPS) parameters of the same $Al_{65}Cu_{20}Cr_{15}$ QC powders have been reported in a previous paper [36].

The reaction equation of the complete combustion of propane is as follows:

$$C_3H_8 + 5O_2 = 4H_2O + 3CO_2. \tag{1}$$

According to this equation, the stoichiometric propane–oxygen ratio is 1/5 = 0.2, where the flame enthalpy is maximum. Two spray conditions, reducing (R) and oxidizing (O), were used. Reducing condition was propane rich and oxidizing was oxygen rich. Since 20% oxygen is present in the high-pressure air used to transport the feedstock powders, the fuel-oxygen ratios of the reducing and oxidizing flame were set at 0.204 and 0.196 respectively, as listed in Table 1. The thickness of the as-sprayed coatings ranged from 200 to 900 µm.

2.2. Composition and structure examination

X-ray diffraction (XRD) was done using an X-ray diffractometer (Rigaku D/MAX-Ultima +/PC) with a Cu anode ($\lambda = 0.15406$ nm). A Philips XL30 scanning electron microscope (SEM) was used to characterize the topographic morphologies of the feedstock and coatings, and the Al and O contents in the coatings were estimated by its energy dispersive X-ray spectroscopy (EDS). The coating cross sections were observed and photographed by an Olympus GX51F computerized light microscope, whose Olycia M3 software was used to evaluate the coating porosity. A MH-6 hardness tester was used to measure the

Coating code	Powder	Particle size (µm)	Feed rate (g/min)	Compressed air flow (L/min)	Propane flow (L/min)	Oxygen flow (L/min)	Fuel–oxygen ratio	Spray distance (mm)
HF1 (R)	Al ₆₅ Cu ₂₀ Cr ₁₅	61-74	10	256	53	208	0.204	180
HF2 (0)	Al ₆₅ Cu ₂₀ Cr ₁₅	61-74	10	262	58	243	0.196	180
HF3 (0)	Cu180	44-61	32	262	58	243	0.196	180

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