

Article



# Phase Transformation of High Velocity Air Fuel (HVAF)-Sprayed Al-Cu-Fe-Si Quasicrystalline Coating

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**Abstract:** Al-Cu-Fe-Si quasicrystalline coatings were prepared by high velocity air fuel spraying to study their phase transformation during the process. The feedstock powder and coating were phase characterized by scanning electron microscopy, X-ray diffractometry, differential scanning calorimetry, and transmission electron microscopy. Results show that  $Al_3Cu_2$  phase, a small amount of  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub> phase, quasicrystalline phase (QC), amorphous phase, and  $\beta$ -Al (Cu, Fe, Si) phase were present in the sprayed  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  powder. For a typical flattened powder particle, the splat periphery was surrounded by a 1 µm thick amorphous phase. The inside area of the splat was composed of the QC covered by the  $Al_3Cu_2$  and Si-rich  $\beta$ -Al (Cu, Fe, Si) phases. Another kind of Curich  $\beta$ -Al (Cu, Fe, Si) phase can be found close to the amorphous area with a similar composition to the original  $\beta$ -Al (Cu, Fe, Si) phase in the powder. Different phases were observed when the periphery and inside area of the splat were compared. This result was caused by the difference in the heating and cooling rates.

**Keywords:** high velocity air fuel spraying; Al-Cu-Fe-Si quasicrystal alloy; quasicrystalline coating; amorphous phase; phase transformation

## 1. Introduction

A solid state between crystalline and non-crystalline solids, which was later identified as a quasicrystal, was first reported in a rapidly solidified Al-Mn alloy [1]. In terms of atomic structure, quasicrystals have a long-range atomic arrangement similar to crystals but exhibit fivefold axis symmetries, which cannot exist in classical crystallography. This class of material exhibits excellent properties, such as low surface energy [2,3], low electrical and thermal conductivity [4,5], remarkable optical properties [6], good wear resistance [7], high resistance to oxidation [8], and corrosion [9]. Despite their excellent performance, the applications of quasicrystal alloys as structural materials are limited by their intrinsic high brittleness and poor deformability at room temperature. This drawback can be ignored by applying thin coatings as a functional layer onto substrates that bear load [10].

Quasicrystals are commonly prepared via conventional solidification of molten alloys, melt spinning, mechanical alloying, physical vapor deposition (PVD), and gas atomization [11]. Cast ingot, ribbon, film, and powder can be obtained with different spatial scales, suggesting distinct solidification rates. Existing studies have mainly focused on the microstructure, phase transformation, and property of quasicrystals prepared by conventional casting, melt spinning [12], mechanical alloying [13,14], and PVD [15,16]. The microstructure and phase composition of gas- atomized quasicrystalline powder have been rarely studied. As a spraying feedstock material, gas-atomized powder is often used because of its low oxidation rate and good flowability.

In recent years, high velocity air fuel (HVAF) spraying has received considerable attention for its extremely fast particle speed and relatively low temperature, which are advantageous for the

deposition of amorphous [17,18] and quasicrystalline coatings. In the present study, Al-Cu-Fe-Si quasicrystalline coatings were prepared by HVAF. The phase transformation from the gas-atomized feedstock powder to a quasicrystalline coating during spraying was investigated. Al-Cu-Fe family quasicrystal has always been a hot research topic given its low cost and nontoxicity [19,20]. On the basis of the Al-Cu-Fe system, some researchers have tried to use semi-metal elements such as Si, B to replace Al element. It was found that the QC formation domain can be expanded by the addition. Among them, the  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  alloy showed a relatively high hardness and fracture toughness compared to the other Si containing Al-Cu-Fe alloys [21] Thus,  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  gas-atomized powder was selected as spraying material. The findings of this study may provide references for the process control of HVAF-sprayed quasicrystalline coating deposition.

#### 2. Materials and Methods

#### 2.1. Fabrication of Al-Cu-Fe-Si Quasicrystalline Coating

Gas-atomized powder with the nominal chemical composition of  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  was used in the present study, which was commercially available. The powders were dried at 80 °C in an oven for 1 h and sieved in the range of 25–38 µm for spraying. The quasicrystalline coating was deposited on a 5052 aluminum alloy with a dimension of 40 mm × 40 mm × 10 mm. Before spraying, the substrate was cleaned with ethanol in an ultrasonic bath. The cleaned substrates were grit-blasted using a 180-mesh alumina grit to obtain a rough surface.

The AK02T HVAF spraying system manufactured by Kermetico Inc. (Benicia, CA, USA) was applied to prepare the quasicrystalline coating. Propane and nitrogen were selected as the fuel gas and carrier gas, respectively. The powders were heated and accelerated by the combustion of fuel gas and compressed air. Table 1 shows the specific spraying parameters.

Parameter	Condition
Particle size (µm)	25–38
Spraying speed (m/s)	1.5
Propane pressure (MPa)	0.6
Air pressure (MPa)	0.5
Carrier gas $N_2$ (l/min)	35
Stand-off distance (mm)	210
Particle size (µm) Spraying speed (m/s) Propane pressure (MPa) Air pressure (MPa) Carrier gas N <sub>2</sub> (l/min) Stand-off distance (mm)	25–38 1.5 0.6 0.5 35 210

Table 1. Spraying parameters.

#### 2.2. Powder and Coating Characterization

The phase composition of powder and the as-sprayed coating was investigated by X-ray diffraction (XRD) on a RIGAKU D X-ray diffractometer (Rigaku International Corporation, Tokyo, Japan) by using Cu Kα radiation with 2θ diffraction angle ranging from 10° to 90° and a scanning speed of 5°/min. The morphologies of the powder and the cross section microstructure of the as-sprayed coating were observed by scanning electron microscopy (SEM) through a Quanta 200FEG instrument (FEI Company, Hillsboro, OR, USA). The microstructure of the powder and the as-sprayed coating was analyzed via transmission electron microscopy (TEM) by using a FEI Talos F200 transmission electron microscope (Shanghai Yuzhong Industrial Co., Ltd., Shanghai, China). The TEM instrument was coupled with a Brucker Quantax 400 energy-dispersive X-ray spectroscopy (EDS) device for composition measurement. The TEM samples were prepared by focused ion beam (FEI Quanta 3D). The MDSC-Q100 Differential scanning calorimetry (DSC, TA, New Castle, DE, USA) was performed from room temperature to 1200 °C at a heating rate of 20 K/min to detect phase transformation.

## 3. Results and Discussion

#### 3.1. Characterization of Feedstock

The feedstock powder was characterized using SEM, DSC, and XRD to confirm the phase composition and analyze the phase transformations during HVAF. The results are shown as follows.

The powder should have a good flow performance to maintain continuous and stable powder feeding during spraying. As shown in Figure 1a, most particles have good sphericity and smooth surface. Small amounts of crushed particles were found because of the post-atomization effect, and this result is related to the brittleness of the quasicrystal.

Figure 1b presents the XRD patterns obtained from the feedstock powder ranging from 25  $\mu$ m to 38  $\mu$ m. After qualitative analysis with Jade 6.5, five kinds of phases were confirmed. They are Al<sub>3</sub>Cu<sub>2</sub> whose prototype [22] is Ni<sub>2</sub>Al<sub>3</sub>, CsCl type  $\beta$ -Al (Cu, Fe, Si),  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub>, QC, and amorphous phases. The XRD patterns suggest that certain crystallization peaks developed on the steamed "bread" peak, consistent with the TEM results which will be discussed later.



Figure 1. (a) SEM morphology and (b) XRD results of gas-atomized Al<sub>50</sub>Cu<sub>20</sub>Fe<sub>15</sub>Si<sub>15</sub> powder.

Figure 2a presents the DSC curves of the gas-atomized  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  powder containing one exothermic peak and three endothermic peaks. The exothermic peak is the combination of amorphous crystallization and  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub> decomposition. The heat release during crystallization of amorphous phase is in a dominant position. The other three endothermic peaks were associated with the decomposition of  $\beta$ -Al (Cu, Fe, Si) (740–840 °C), QC (850–920 °C), and Al<sub>3</sub>Cu<sub>2</sub> (930–1000 °C) phases. Karakose and Keskin [23] reported similar results while studying the phase formation of melt-spun Al<sub>64</sub>Cu<sub>20</sub>Fe<sub>12</sub>Si<sub>4</sub> alloy quenching at 25 m/s. The  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub> (635 °C, peak),  $\beta$ -AlFe (776 °C, peak), and Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> (840 °C, peak) QC phases were detected. The endothermic peak of the  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub> phase could not be detected in Figure 2a because of compensation from amorphous crystallization. Similarly, Wang et al. [24] discovered an exothermic peak at approximately 550 °C on the differential thermal analysis and DSC curves of the Al<sub>52</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub>Si<sub>10</sub> alloy quenched at 2400 rpm; this finding was caused by the existence of the amorphous phase. The peak position of  $\beta$  and QC were close but negligibly different owing to the difference in their Si contents and cooling rates. The atomized and sieved powder (25 µm to 38 µm) could experience faster cooling compared with ribbons with thickness of  $37-135 \mu m$ , thereby explaining the absence of an amorphous phase in the melt-spun Al<sub>64</sub>Cu<sub>20</sub>Fe<sub>12</sub>Si<sub>4</sub> ribbons. Annealing of powder with different sizes was carried out at 750 °C/12 h to further confirm their phase composition and consistency with the DSC curve. The  $\beta$  phase was decomposed when the temperature reached 750 °C. As shown in Figure 2b, the bottom line of the pattern became straight without the steamed "bread" character after annealing at 750 °C for 12 h, suggesting the crystallization of the amorphous phase. QC was dominant with a small amount of  $\beta$ -Al

(Cu, Fe, Si) phase. XRD patterns of different sizes were nearly the same after annealing at 750 °C/12 h, suggesting the consistency of composition between coarse and fine powders.



**Figure 2.** (a) DSC results of  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  powder measuring 25 µm to 38 µm; (b) XRD curves for the annealing of  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  powder sieved with different mesh size at 750 °C/12 h.

TEM was conducted to further investigate the microstructure of the feedstock. As shown in the HAADF image (Figure 3c), three areas with different contrasts can be detected. Figure 3a,b show the SAED pattern of the  $\beta$ -Al (Cu, Fe, Si) phase along the [001] and [012] zone axes, respectively. Table 2 lists the EDS results on three particular particles. The composition of  $\beta$ -Al (Cu, Fe, Si) phase was 49.72 at% Al, 22.76 at% Fe, 12.01 at% Cu, and 15.52 at% Si, suggesting that 27.53 at% Fe was replaced by Cu and Si (up to 90% Fe can be replaced by Cu in the  $\beta$ -AlFe phase [25]). The EDS result suggests that particle 3 comprise 58.13 at% Al, 37.99 at% Cu, 3.88 at% Fe, and a small amount of Si, which was identified as the Al<sub>3</sub>Cu<sub>2</sub> phase. Figure 3d shows the typical diffraction ring of the amorphous phase. Unfortunately, the diffraction pattern of QC cannot be found in this TEM sample, which could be explained by the fact that the particle belongs on the finer side in the feedstock powder. Combining the XRD and DSC results, the QC phase and amorphous phase were considered to coexist in the feedstock powder with different sizes. The  $\beta$ -Al (Cu, Fe, Si) phase coexisted with the QC and amorphous phase; Lee et al. [21] studied the effects of Si addition to the QC phase on a melt- spun  $Al_{65}Cu_{20}Fe_{15}$  alloy; when the Si content was increased up to 15% (the same composition described as the current work), the 1/1 cubic approximant phase was formed rather than the genuine QC phase with the coexistence of  $\beta$ -Al (Cu, Fe, Si) phase. Given its more rapid cooling rate than that of melt-spinning [11], the QC and amorphous phases rather than the 1/1 cubic approximant phase existed in the gas-atomized Al<sub>50</sub>Cu<sub>20</sub>Fe<sub>15</sub>Si<sub>15</sub> powder. Quivy et al. [26] also reported the coexisting phase in the melt-spun  $Al_{55}Cu_{25,5}Fe_{12,5}Si_7$  alloy; however, the coexisting phase was the QC phase accompanied by a small amount of  $\beta$ -Al (Cu, Fe, Si) phase. In conclusion, the phase composition of Al-Cu-Fe-Si series alloy was considerably affected by the Si content and cooling rate related to the manufacturing process.

Remark	Phase	Percent	Al	Fe	Cu	Si
Particle 1	Amorphous	at%	54.93	17.97	10.05	17.05

at%

at%

β-Al (Cu, Fe, Si) phase

Al<sub>3</sub>Cu<sub>2</sub> phase

Particle 2

Particle 3

Table 2. EDS results of different powder phases.

49.72

58.13

22.76

3.88

12.01

37.99

**Total** 100

100

100

15.52

0.15



**Figure 3.** (a) Selected area electron diffraction (SAED) pattern of the CsCl type  $\beta$ -Al(Cu, Fe, Si) phase along the [001] zone axis; (b) SAED pattern of the  $\beta$ -Al(Cu, Fe, Si) phase along the [012] zone axis; (c) high-angle annular dark-field imaging (HAADF) image of Al<sub>50</sub>Cu<sub>20</sub>Fe<sub>15</sub>Si<sub>15</sub> powder; (d) diffraction pattern of the amorphous phase.

Element maps of feedstock powder were completed to show the transport of elements during spraying (Figure 4). Al was evenly distributed in all phases, and Cu mainly existed in the  $Al_3Cu_2$  phase with a small amount in other phases. Almost all the Si was evenly distributed in the QC, amorphous, and  $\beta$ -Al (Cu, Fe, Si) phases.



**Figure 4.** Element maps of feedstock powder, measured by EDS equipped in TEM (**a**) Al; (**b**) Cu; (**c**) Fe; (**d**) Si.

Figure 5a shows the SEM image from a cross section of the coating. The coating thickness was approximately 240  $\mu$ m. Figure 5c shows the XRD pattern of the spraying coating. A broad diffraction peak was observed compared with the original feedstock powder, which was considered to be the result of the increasing amorphous phase. Aside from the broadened diffraction peak, the QC and  $\beta$ -Al (Cu, Fe, Si) phase peaks can be found with a small amount of Al<sub>3</sub>Cu<sub>2</sub> and  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub> phases. Figure 5d shows the XRD results of the coating after 750 °C/12 h and 950 °C/12 h of annealing. Similar to the powder, the coating annealed at 750 °C/12 h exhibited QC and  $\beta$ -Al (Cu, Fe, Si) phases. This result suggests that no evident Al loss was detected during spraying, which is a remarkable advantage for the manufacturing of the Al-Cu-Fe series quasicrystalline coating. When the annealing temperature reached 950 °C, the QC and  $\beta$ -Al (Cu, Fe, Si) phases transformed to a high-temperature Al<sub>3</sub>Cu<sub>2</sub> phase. After slow cooling, the Al<sub>3</sub>Cu<sub>2</sub> phase was retained.

The SEM image of coating in high magnification (Figure 5b) showed two obvious contrasts layer by layer, which should be explainable by the coating formation of thermal spraying. During spraying, feeding powder was heated and accelerated to obtain melted or semi-melted particles with high kinetic energy, then flattened and stacked layer by layer to form the final coating. To further analyze the phase composition of the contrast difference, TEM, SAED, and mapping were conducted. Figure 6a shows the TEM overview image of the coating sample, in which two layers of different contrasts can also be observed, which were caused by the contrast of amorphous and other phases. The yellow dotted line shown in Figure 6a is considered to be the part of splat. Figure 6b,c shows the HADDF image and mapping of the same area, respectively. The overall structure appeared similar to a "sandwich," and the amorphous phase occupied the top and bottom areas, as confirmed by the diffraction ring shown in Figure 7. QC, Al<sub>3</sub>Cu<sub>2</sub> phase, and two kinds of  $\beta$ -Al (Cu, Fe, Si) phases were observed in the middle area. QC phase was surrounded by the  $Al_3Cu_2$  phase. As shown in Figure 7, the electron diffraction patterns of the QC phase exhibited two-, three-, and fivefold symmetries. Table 3 shows the EDS results of different phases in the coating. The composition of QC phase is almost the same as that of amorphous phase in the powder, suggesting that some QC phase is generated from the transformation of the amorphous phase in the center of the flattened particle. Compared with the periphery of splat, the center has a suitable heating and cooling rate for the formation of the quasicrystalline phase. The compositions of two  $\beta$ -AlFe phases found in the coating are as follows: the Si-rich phase was composed of 48.74 at% Al, 19.07 at% Fe, 3.22 at% Cu, and 28.97 at% Si distributed in the Al<sub>3</sub>Cu<sub>2</sub> phase; the Cu-rich phase consisted of 49.84 at% Al, 21.28 at% Fe, 16.84 at% Cu, and 12.04 at% Si located near the amorphous phase. This position is attributed to the  $\beta$ -Al (Cu, Fe, Si) phases of the particle surface that might have broken away after melting of the amorphous or QC phase. However, the phases might have had inadequate time to melt before impact on the substrate and were retained near the amorphous phase. The phase distribution and chemical composition of powder suggest that approximately 3.5 at% Si was replaced by Cu in Cu-rich  $\beta$ -Al (Cu, Fe, Si) phase, and most Cu with a small amount of Fe was replaced by Si to form a Si-rich  $\beta$ -Al (Cu, Fe, Si) phase. The in-flight particle was heated and accelerated. Given its comparatively low temperature and high velocity, the in-flight particle was semi-melted before impacting the base. Compared with the inside of the in-flight particle, its periphery had a faster cooling rate and formed an amorphous phase easily. Several original  $\beta$ -Al (Cu, Fe, Si) phases near the splat periphery were released from the amorphous or quasicrystalline phase to form a new Cu-rich  $\beta$ -Al (Cu, Fe, Si) phase. Inside the in-flight particle, the amorphous had adequate time to grow on the QC phase, and the original β-AlFe phase inside was released to become Si-rich  $\beta$ -Al (Cu, Fe, Si) phase when the splat formed.



**Figure 5.** XRD pattern and SEM image of the high velocity air fuel (HVAF)-sprayed  $Al_{50}Cu_{20}Fe_{15}Si_{15}$  coating. (a) Cross section SEM image in SE mode; (b) diagram of flattened particle in BSE mode; (c) XRD pattern of spraying coating; (d) XRD pattern of the coating annealed at 750 °C/12 h and 950 °C/12 h.



**Figure 6.** (a) Overview of coating sample for TEM investigation; (b) HAADF images of the amorphous and quasicrystalline phase (QC) areas; (c) Si-Cu-Fe maps related to (b).



**Figure 7.** SAED pattern of QC in the coating obtained along the twofold, threefold, and fivefold axes; diffraction pattern of the amorphous phase.

Table 3. EDS results of different pha	ases in the coating.
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Phase	Percent	Al	Fe	Cu	Si	Total
QC	at%	55.00	17.48	9.88	17.64	100
Amorphous	at%	55.17	12.38	17.48	14.98	100
β-Al (Cu, Fe, Si), Cu-rich	at%	49.84	21.28	16.84	12.04	100
β-Al (Cu, Fe, Si), Si-rich	at%	48.74	19.07	3.22	28.97	100

#### 4. Conclusions

Al-Cu-Fe-Si coatings containing QC and amorphous phases were prepared on an aluminum alloy with a thickness of approximately 240  $\mu$ m. The feedstock powder was composed of the Al<sub>3</sub>Cu<sub>2</sub> phase whose prototype is Ni<sub>2</sub>Al<sub>3</sub>, CsCl type  $\beta$ -Al (Cu, Fe, Si),  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub>, QC and amorphous phases. The QC phase and amorphous phase exist in the particles of different sizes. The amorphous phase tends to be in the finer range of the feedstock powder. The  $\beta$ -Al (Cu, Fe, Si) phase coexisted with the amorphous or quasicrystalline phase.

The splat periphery was amorphous phase and approximately 1  $\mu$ m thick. The center area of splat was composed of QC phase covered by Al<sub>3</sub>Cu<sub>2</sub> and Si-rich  $\beta$ -AlFe phases. Another kind of Cu-rich  $\beta$ -Al (Cu, Fe, Si) phase can be found close to an amorphous area, which has a similar composition to the original  $\beta$ -Al (Cu, Fe, Si) phase in the powder.

The final phase composition of HVAF-sprayed quasicrystalline coating was greatly affected by the original phase of the feedstock powder and the cooling rate when there was splat formation.

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