MICROSTRUCTURAL EVOLUTION, OXIDATION AND WEAR OF Al-Cu-Fe
QUASICRYSTALLINE COATINGS

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ABSTRACT

Plasma arc sprayed coatings were prepared with two different size fraction starting powders having a nominal composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$. Powders were obtained by crushing a cast ingot and by gas atomization. Coatings were characterized by electron microscopy, X-ray diffraction and chemical analysis. Oxidation tests were performed in dry oxygen at 500° and 700°C. Finer powders produced coatings with more of the cubic phase than coatings formed with coarser powders. The as-sprayed coatings developed different phases during oxidation. Wear tests of as-sprayed coatings were performed over a range of temperatures in a pin-on-disc arrangement against aluminum oxide. The coefficient of friction increased from around 0.44 at room temperature to near 0.60 at 600°C. Differences in wear behavior of the coatings were seen as a function of temperature.

Introduction

Since the remarkable identification of quasicrystalline structures by Shechtman over ten years ago, many studies have been performed to further unravel the structures and physical properties of these unique materials.¹⁻³ More recently, researchers have begun to investigate the application of quasicrystalline coatings due to their potential wear and corrosion resistance. Most of these latter studies have focused on Al-Cu-Fe alloys deposited by thermal spraying techniques such as plasma arc spraying (PAS). Several reports have shown that Al-Cu-Fe quasicrystalline coatings have low coefficients of friction in dry sliding and possess good oxidation and corrosion resistance.^{4,5} There is, however, a lack of related literature describing the effects of PAS processing parameters on coating microstructures and properties. The objectives of this work are to observe the influence of starting powders on coating structures and to examine the oxidation and wear behavior of Al-Cu-Fe coatings.

Experimental Procedure

Starting Powder

Starting powders with a composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ were prepared by two techniques. One batch was obtained by crushing a 50 mm diameter ingot prepared by induction melting of the pure elements (purity >99.99%) in an argon atmosphere. The other powder was formed by gas atomization of a superheated melt of the pure elements (purity >99.99%) with argon. The cast and crushed and gas atomized powders were split into different size distributions for PAS. A fine fraction between 25 and 45 μm and a coarse fraction between 45 and 75 μm were separated from both powders by air classification and screening, respectively. In addition, a narrower cut of powder between 53 and 58 μm was screened from the coarser fraction to form the coatings used in the wear tests.

Plasma Arc Spraying Parameters

All coatings in this study were prepared with the same plasma gun operating parameters under atmospheric conditions. These details are discussed elsewhere.⁶ Coatings were deposited onto preheated stainless steel substrates and substrates at ambient temperature. Preheating was achieved by running the plasma gun without powder over the surface of the substrate; surface temperatures were approximately 225°C when coating commenced. Relatively thick (e.g., 1 mm) coatings were formed and then removed from the substrate after cooling. Samples for microstructural analysis and oxidation tests were cut from the coatings. In the following, the symbols *C* and *G* will define powder produced by crushing a cast ingot and by gas atomization,

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respectively, whereas letters *f* and *c* will stand for fine (25 to 45 μm) and coarse (45 to 75 μm) size fractions of starting powders. The approximate temperature of the substrate prior to coating will be labeled as *a* for ambient temperature and *h* for pre-heating. For example, a coating formed by spraying with 25 to 45 μm cast and crushed powder onto an ambient temperature substrate will be labeled *Cfa*.

Coating Evaluation

Chemical analysis of as-sprayed coatings was performed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Oxygen contents of as-sprayed and oxidized coatings were determined by inert gas fusion. Structural analysis was carried out on powdered coating samples using X-ray powder diffraction (XRD) with $\text{CuK}\alpha$ radiation between 42° and 46° two-theta. Microstructures of as-sprayed and oxidized coatings and wear surfaces of pins and discs were observed using scanning electron microscopy (SEM). Localized phase chemistry of one oxidized coating was determined by electron microprobe spectroscopy (EMP). Characterization of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ cast ingots and gas atomized powders has been reported elsewhere.⁶

Oxidation tests of coating samples were run in flowing O_2 (50 ml min^{-1}) at 500° and 700°C . Samples were approximately $1 \times 1 \times 10$ mm bars cut from sprayed coatings. Two bars from each coating were ground and polished to a 9 μm finish and then degassed under vacuum at 200°C overnight before testing. Weight gains during oxidation were measured after removing the samples from the furnace at 24, 48 and 144 hours. One coating sample (*Gca*) was oxidized at 700°C under flowing dry oxygen for 225 hours in a furnace equipped with a microbalance for continuous weight gain measurement. In addition, a sample of each as-sprayed coating was annealed at 700°C for two hours under vacuum (10^{-6} mbar).

The wear behavior of PAS coatings formed with +53, -58 μm gas atomized powder was examined by running pin-on-disc sliding wear tests at 25° , 200° , 400° and 600°C . In this experiment the discs were stainless steel substrates preheated to 225°C and then coated with the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder. The pin was Al_2O_3 and was machined with a 3 mm radius hemispherical end. Coatings were ground and polished to a 9 μm finish, and the pins were lightly ground with 600 grit emery paper before each test. Sliding was performed in a track diameter of 40 mm and sliding velocity was held constant at 0.1 m s^{-1} . The normal load applied to the pin was 1.5 kg. Frictional forces were determined from strain measurements which were taken at intervals during each 20 minute test. Two coated discs were tested at each temperature.

Results and Discussion

The cast and crushed powder was far less homogeneous than the gas atomized powder due to the contrasting solidification rates. Although not displayed here, average phase segregation of the central portion of the cast ingot was on the order of 50-100 μm . Since the ingot was crushed into particles ranging from 25 to 75 μm , this scale of segregation was sufficient to yield individual particles with differing compositions and structures. All powders contained the icosahedral (ψ), cubic (β) and monoclinic (λ) phases⁶.

The differences in homogeneity of the two different starting powders is clearly visible in the PAS coatings formed from them. The as-sprayed microstructures of coatings *Cfa*, *Cca*, *Gfa* and *Gca* are shown in Figures 1a, 2a, 3a and 4a, respectively. The cast and crushed powder coatings still retain some of the segregated structure of the original cast ingot. This is particularly evident in the coating formed with the +45, -75 μm cast and crushed powder (*Cca*). The large dark regions are the monoclinic λ phase, which was the primary solidification phase. The blocky morphology of this phase suggests that all the starting powders were not completely melted during spraying (i.e., these are partially unmelted particles). Further evidence that the plasma spraying parameters used to form these coatings were not optimized can be seen in the microstructure of the *Gca* coating (Fig. 4d). Regions within the coating still exhibit a typical gas atomized particulate solidification microstructure.⁶ There were very few unmelted particles in the *Gfa* coating and the chemistry appears to be uniform (Fig. 3a). Microstructures of corresponding cast and crushed and gas atomized coatings deposited onto hot substrates follow the same trends with respect to chemical homogeneity and particles melting, but are less porous. This latter effect may be due to improved particle deformation during impact.

Figure 1. Backscattered electron images of (a) as-sprayed, (b) 500°C oxidized and (c) 700°C oxidized coatings formed with +25, -45μm cast and crushed powder coatings deposited onto ambient temperature substrates (*Cfa*).

Figure 2. Backscattered electron images of (a) as-sprayed, (b) 500°C oxidized and (c) 700°C oxidized coatings formed with +45, -75μm cast and crushed powder coatings deposited onto ambient temperature substrates (*Cca*).

Figure 3. Backscattered electron images of (a) as-sprayed, (b) 500°C oxidized and (c) 700°C oxidized coatings formed with +25, -45μm cast and crushed powder coatings deposited onto ambient temperature substrates (*Gfa*).

Figure 4. Backscattered electron images of (a) as-sprayed, (b) 500°C oxidized and (c) 700°C oxidized coatings formed with +45, -75μm cast and crushed powder coatings deposited onto ambient temperature substrates (*Gca*).

Chemical analysis of as-sprayed coatings shows that the fine fractions of particles tend to lose aluminum and pick up more oxygen during spraying than the larger fractions (Table 1). These results were seen with both cast and crushed and gas atomized starting powders. The loss of aluminum with the fine fraction powders appears significant enough to adjust the phase equilibrium of the solidified coatings. Comparison of the solid curves in Figure 5 shows a reduced fraction of the quasicrystalline ψ phase in the coatings sprayed with the fine fraction powders. Although not shown here, the coatings deposited onto the heated substrates have slightly higher ψ phase contents than the corresponding ambient temperature substrate coatings. The reduced quench rate of particles solidifying onto the heated substrate may provide extended time for the liquid to pass through the higher temperature β and λ phases into the ψ stability domain.

Oxidation of Plasma Arc Sprayed Coatings

Weight gains during oxidation at 500° and 700°C of 1x1x10 mm bars cut from coatings sprayed with gas atomized powders are displayed in Figure 6. Data from cast and crushed coating samples are not presented here but display very similar behavior. Surface area was calculated from sample geometry. However, these values are artificially low because the bars had a fraction of open porosity and some surface-connected cracks. No consistent trends in weight gains were seen as a function of either powder type or size; scatter in the data may be due to differences in actual surface areas of individual samples. The coatings deposited onto the hot substrates tended to stop gaining weight after 48 hours, while the ambient temperature substrate coatings showed slight weight increases between 48 and 144 hours. This may be due to the higher porosity of coatings deposited onto the ambient temperature substrates, but further analysis is required. Bulk oxygen values were determined from several as-sprayed coatings and samples oxidized at 700°C (Table 1). These values are comparable to the increases calculated from the weight gain data measured at 700°C (Fig. 6).

A parallel oxidation study was performed at 700°C under flowing O₂ with a *Gca* coating which was first annealed to single-phase Ψ at 700°C in vacuum. Tests were conducted in a furnace equipped with a microbalance for continuous measurement of weight gain. The results are included in Figure 6. This sample was approximately 1x5x10 mm and was polished similarly to the bars discussed earlier. Again, sample porosity and surface cracks make the specific weight gain data suspect. The values measured with the *Gca* coatings during the two oxidation tests at 700°C are comparable. The continuously measured weight gains initially show linear behavior followed by parabolic kinetics with a reaction index of approximately 1.9. Qualitatively, the weight gains show similar diffusion controlled behavior, which suggests that Al-Cu-Fe PAS coatings are resistant to excessive oxidation in dry O₂.

The PAS coatings developed several interesting features during oxidation at elevated temperatures for 144 hours. Microstructures of *Cfa*, *Cca*, *Gfa* and *Gca* coatings oxidized at 500°C are shown in Figures 1b, 2b, 3b, and 4b, respectively. At 500°C, the fine fraction gas atomized coatings develop a thin phase predominantly along the splat boundaries. This is seen as lighter areas on the backscattered electron micrographs (Fig. 3c). The *Gca* coatings do not show the same splat boundary features, but do exhibit similar features in areas which contained unmelted particles (Fig. 4b). The broad inhomogeneities of the *Cfa* and *Cca* coatings make evaluation of the oxidized microstructures difficult using only SEM. These coatings do appear to show some higher atomic number contrast, but no compositional determinations were made. The two-theta values of individual XRD patterns were shifted using the Ψ peaks as an internal standard. The XRD results clearly show a phase evolution of the as-sprayed coatings during the 500°C oxidation tests. The gas atomized powder coatings have a shoulder on the right-hand side of the (110) β peak. It is not clear whether this results from diffraction from the λ phase or is from a new β phase with a composition different than the β phase producing the higher intensity peak. Similar results are seen with the cast and crushed powder coatings oxidized at 500°C, but the fraction of the new phase is higher.

The 700°C oxidized coatings are displayed in Figures 1c, 2c, 3c and 4c, respectively. The gas atomized powder coatings have developed two distinct phases within the surrounding matrix. This is clearly seen in Figure 4c. The vacuum annealed single-phase Ψ *Gca* sample oxidized at 700°C during the continuous weight gain measurement experiment shows a very similar microstructure to the as-sprayed *Gca* coating oxidized at 700°C (Fig. 4c). Chemical analysis by EMP of the three phases in the 700°C oxidized *Gca* coating shows that the matrix is Al₆₂Cu₂₅Fe₁₂.

Table 1. Coating descriptions and chemical analysis of plasma arc sprayed coatings.

Label	Coating Sample			As-sprayed				700°C oxidized
	Starting powder	Particle size (μm)	Substrate Temperature (°C)	Al	Cu	Fe	O	O (weight %)
<i>Cfa</i>	cast & crushed	+25,-45	~25	40.6	40.4	17.7	1.4	2.2
<i>Cfh</i>	cast & crushed	+25,-45	~225	40.4	40.8	17.6	1.5	2.2
<i>Cca</i>	cast & crushed	+45,-75	~25	42.4	41.8	15.3	-	-
<i>Cch</i>	cast & crushed	+45,-75	~225	42.6	40.8	15.5	-	-
<i>Gfa</i>	gas atomized	+25,-45	~25	41.2	40.5	17.4	-	-
<i>Gfh</i>	gas atomized	+25,-45	~225	41.2	40.1	17.1	-	-
<i>Gca</i>	gas atomized	+45,-75	~25	42.9	39.8	16.9	0.5	1.3
<i>Gch</i>	gas atomized	+45,-75	~225	42.8	40.1	17.2	0.3	1.3

*Composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ in weight % is approximately 42.3% Al, 40 w/o Cu, 17.7 w/o Fe.

Figure 5. X-ray powder diffraction patterns of as-sprayed, oxidized and vacuum annealed coatings which were deposited onto ambient temperature substrates with the following powders: (a) fine cast and crushed powder *Cfa*, (b) coarse cast and crushed powder *Cca*, (c) fine gas atomized powder *Gfa*, and (d) coarse gas atomized powder *Gca*.

the light phase is $\text{Al}_{51}\text{Cu}_{39}\text{Fe}_{10}$ and the dark phase is $\text{Al}_{72}\text{Cu}_6\text{Fe}_{22}$. Oxygen was not included in this spectroscopic analysis, but may likely be part of these phases.⁴ The matrix and dark phase compositions are the Ψ and λ phases, respectively.⁶ The light phase composition falls within the β phase region, but is a different composition than the usual $\text{Al}_{55}\text{Cu}_{41}\text{Fe}_4$ composition seen in the isostructural cubic phase region in the Al-Cu-Fe system.⁷ The relatively higher Cu and Fe contents of the β phase formed in this study produce a lattice expansion, as evidenced by the peak at a lower two-theta value. The calculated lattice parameter for the (110) β peak in Figure 4c is 2.9437Å, which is in excellent agreement with the value reported for similar compositions.⁸ It is more difficult to extract XRD evidence of the λ phase due to the numerous scattering planes of the monoclinic system; however, peaks corresponding to several high intensity scattering planes were observed. Apparently the localized compositional shifts which occurred during oxidation at 700°C perturb the phase equilibrium of the system and cause even a single-phase Ψ microstructure to partially decompose into β and λ structures.

Microstructures of the cast and crushed powder coatings oxidized at 700°C show some refinement of the phases present in the as-sprayed and 500°C oxidized coatings. After the 700°C oxidation tests, the *Cfa* coatings contain more of the β phase and less of the Ψ phase than the *Cca* coatings (Fig. 5). The cast and crushed powder coatings all have less of the Ψ phase than the corresponding coatings formed with the gas atomized powders. This is most likely due to the higher initial fraction of the Ψ phase and the increased uniformity of the gas atomized powders.

Samples of each as-sprayed coating were annealed in vacuum at 700°C for two hours. The XRD results are displayed in Figure 5. All coatings sprayed with the +45, -75 μm powders annealed to nearly single-phase Ψ . The compositional changes and oxidation of the +25, -45 μm powders during spraying appears to impact the phase changes during vacuum annealing. The finer fraction powder coatings still contain some of the β phase after the two hour treatment; however, the coarser fraction powder coatings are close to single-phase Ψ . Despite the chemical inhomogeneity of the *Cca* powder coatings (Fig. 2a), they too form a nearly single-phase microstructure after vacuum annealing. However, the *Cfa* powder coatings still have a substantial fraction of the β phase after the same treatment. Analogous behavior was observed with the gas atomized powder coatings. The chemical analysis results and these findings suggest that the loss of Al during spraying with the finer powders may have shifted the overall composition out of the single-phase Ψ domain. Also, the accelerated oxidation of the finer powders during spraying may have resulted in a thicker oxide layer around the splat boundaries which could retard the formation of the Ψ phase during solid state annealing or consume Al and produce localized compositional variations. Comparing the collection of XRD patterns shown in Figure 5 illustrates the higher Ψ phase contents of coarser powder coatings after the oxidizing and vacuum heat treatments.

Wear Behavior of Plasma Arc Sprayed Coatings

The gas atomized PAS coatings formed with the fine fraction powder were low in the Ψ phase, while those prepared with the coarse fraction powder were fairly porous. Therefore, a narrow size fraction of powder between 53 and 58 μm was prepared to spray coatings for wear testing. This compromise was aimed at having a higher Ψ content together with lower porosity. The plasma spraying parameters were kept the same as those used to process the other two size fraction powders. X-ray diffraction results were similar to those obtained from the *Gca* coating (Fig. 5d).

The pin-on-disc tests utilized a pin with a hemispherical end. This configuration develops contact stresses which are much higher than a flat-against-flat testing configuration. The coefficient of friction between the Al_2O_3 pin and the Al-Cu-Fe coatings was measured at different temperatures (Fig. 7). Error bars span the values of the two measurements made with separate coatings at each temperature. The coefficient of friction at the start of the test ranges from around 0.44 at room temperature to near 0.60 at 600°C. These values are higher than other friction data reported for the Al-Cu-Fe system, but the testing configurations are quite different.¹⁰ An increasing coefficient of friction at higher temperatures has generally been observed in sliding experiments with hard materials.⁹ Examination of the wear scars on the coatings and transfer films on the aluminum oxide pin surfaces provide considerable information about the wear behavior of the quasicrystal coating. Figure 8 shows SEM images of the wear scars on the coatings that formed during testing at room temperature and 600°C. The lack of ductility of the Al-Cu-Fe coating at room temperature is seen by the macroscopic cracking and fine-grained wear debris. It

Figure 6. Weight gain versus time for coatings formed with gas atomized powders, as follows: (a) fine powder on ambient temperature substrate *Gfa*, (b) fine powder on heated substrate *Gfh*, (c) coarse powder on ambient temperature substrate *Gca*, and (d) coarse powder on heated substrate *Gch*.

Figure 7. Coefficient of friction with sliding distance.

Figure 8. Secondary electron images of wear scars developed during sliding at (a) 25°C and (b) 600°C and transfer films on Al_2O_3 pins from (c) 25°C and (d) 600°C wear tests.

appears that cracks formed and grew until large areas of material within the wear track were removed. At higher temperatures, the coating material was able to withstand increased plastic deformation. The ability of the coating to flow at 600°C under the developed contact stress resulted in less material removal during sliding than the coatings tested at room temperature (Fig. 8b). However, the increased deformation produces an increase in contact area between the pin and the coatings. This effect may be contributing to an increase in the coefficient of friction at higher temperatures.

The adhesive failure of the coating is further illustrated by observing the material transferred to the Al₂O₃ pin surface (Fig. 8). The transferred material generated during the room temperature test looks like the fine-grained wear debris found in the wear scar of the coating. Conversely, the transfer film on the pin used for the 600°C test is much larger and shows clear signs of plastic flow. In addition, the material on the 600°C pin was well adhered, which indicates that after a period of time the actual sliding that occurred during these tests was coating against coating. Sliding of similar materials against each other is well known to cause unusually high frictional forces. This too may have contributed to the increase in the friction coefficient at higher temperatures. The wear scars and transfer films from the 200° and 400°C sliding tests followed the same trends discussed above.

Conclusion

Plasma arc sprayed Al₆₃Cu₂₅Fe₁₂ coatings prepared with gas atomized powders are chemically more uniform and richer in the quasicrystalline Ψ phase than coatings sprayed with powders obtained by crushing a cast ingot. With the plasma spraying parameters used in this study, starting powders between 25 and 45 μ m tend to lose Al and gain more O during spraying. In general, the coatings are resistant to oxidation at 500° and 700°C in a dry O₂ atmosphere. However, the phase equilibrium of the as-sprayed coatings changes during oxidation tests. In particular, a vacuum annealed, single-phase Ψ coating exhibited localized decomposition to the cubic (β) and monoclinic (λ) phases during oxidation at 700°C. Pin-on-disc tests with an Al₂O₃ pin sliding against an Al₆₃Cu₂₅Fe₁₂ plasma arc sprayed coating produces friction coefficients around 0.44 and 0.60 at room temperature and 600°C, respectively. During sliding at higher temperatures, the quasicrystalline coatings show increased plastic deformation and adhesion to the ceramic pin.

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