IS-T 1753

Synthesis, Characterization and Physical Properties of Al-Cu-Fe
Quasicrystalline Plasma Sprayed Coatings

by

Sordelet, Daniel

PHD Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: November 9, 1995

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RECEIVED
JAN 03 1996
OSTI

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100

TABLE OF CONTENTS

CHAPTER 1: GENERAL INTRODUCTION	1
1. Objective	1
2. Dissertation Organization	1
3. Background	2
4. Summary	13
References	13
CHAPTER 2: EFFECTS OF STARTING POWDERS ON CONTROLLING MICROSTRUCTURAL DEVELOPMENT OF Al-Cu-Fe QUASICRYSTALLINE PLASMA ARC SPRAYED COATINGS	16
Abstract	16
1. Introduction	17
2. Experimental Procedures	18
3. Results	21
4. Discussion	45
5. Conclusions	47
Acknowledgments	48
References	48
CHAPTER 3: PARTICLE SIZE EFFECTS ON CHEMISTRY AND STRUCTURE OF Al-Cu-Fe QUASICRYSTALLINE COATINGS	50
Abstract	50
1. Introduction	51
2. Experimental Procedure	53
3. Results	59
4. Discussion	81

5. Conclusions	88
Acknowledgments	89
References	90
CHAPTER 4: EFFECTS OF BORON ON THE SOLIDIFICATION STRUCTURE OF AN Al-Cu-Fe ALLOY	94
Acknowledgments	116
References	116
CHAPTER 5: MICROSTRUCTURAL EVOLUTION, OXIDATION AND WEAR OF Al-Cu-Fe QUASICRYSTALLINE COATINGS	118
Abstract	118
1. Introduction	119
2. Experimental Procedure	119
3. Results and Discussion	121
4. Conclusions	141
Acknowledgments	142
References	142
CHAPTER 6: MICROSTRUCTURE AND WEAR BEHAVIOR OF QUASICRYSTALLINE THERMAL SPRAYED COATINGS	143
Abstract	143
1. Introduction	144
2. Methods and Materials	147
3. Results and Discussion	148
Acknowledgments	166
References	166
CHAPTER 7: GENERAL CONCLUSIONS	168

CHAPTER 1: GENERAL INTRODUCTION

1. Objective

This research effort focused on plasma arc spraying of Al-Cu-Fe quasicrystalline coatings. The primary objectives were (1) to characterize microstructural development as a function of various processing parameters and (2) to evaluate oxidation and wear behavior. The technological impact of quasicrystals has lagged far behind their revolutionary effect on traditional crystallography. The small amount of published literature on physical properties and tribological behavior of quasicrystals has not emphasized critical aspects of starting materials and processing conditions. Moreover, it remains to be seen if the interesting tribological properties exhibited by quasicrystals (e.g., low coefficients of friction) are due to the quasicrystalline atomic structure, or rather, to secondary effects such as oxide layer formation.

2. Dissertation Organization

The results of this effort are assembled as individual manuscripts. The final product of this work, the Ph.D. dissertation, follows the ISU Graduate College alternate thesis format. The dissertation will consist of five manuscripts which follow a general introduction in Chapter 1. Chapter 2, Effects of Starting Powders on Controlling Microstructural Development of Al-Cu-Fe Quasicrystalline Plasma Arc Sprayed Coatings, examines the effects of starting powder homogeneity on the development of plasma arc sprayed coatings. The following chapter, Particle Size Effects on Chemistry and Structure of Al-Cu-Fe Quasicrystalline Coatings, builds upon the results of Chapter 2 by examining the role of starting powder particle size on coating chemistry and structure. Both of these manuscripts will be published in the *Journal of Thermal Spray Technology*. Chapter 4, Effects of Boron on the Solidification Structure of an Al-Cu-Fe

Alloy, is a brief letter to the *Journal of Materials Science*. It discusses the different solidification structures obtained by adding boron to Al-Cu-Fe materials prepared by various techniques. Note that since Chapter 4 is being submitted as a letter, the condensed format does not use individual section headings within the manuscript. Chapter 5, Microstructural Evolution, Oxidation and Wear of Al-Cu-Fe Quasicrystalline Coatings, has been accepted by the *International Journal of Modern Physics*. This paper includes a discussion of several preliminary tests of oxidation and wear behavior of plasma arc sprayed coatings. The final manuscript, Chapter 6, Microstructure and Wear Behavior of Quasicrystalline Thermal Sprayed Coatings, is a brief paper which will be included in the Proceedings of the *1995 National Thermal Spray Conference*. It is included in the dissertation because it provides some interesting comparisons of quasicrystalline coatings sprayed by techniques other than atmospheric plasma arc spraying. A general conclusion, Chapter 7, is provided to summarize the important conclusions of the individual chapters and to offer suggestions for future studies.

3. Background

3.1 Quasicrystals

3.1.1 Structure

The term "quasicrystalline" is used to describe the structure of materials which have atomic arrangements that violate the strict structural definitions of crystalline matter. Crystalline solids possess long-range positional order with restricted orientational symmetries. The periodicity of a crystal limits the possible rotational symmetries to two-, three-, four- and six-fold rotation axes. In 1984, Schechtman revealed an Al-Mn phase having five-fold rotational symmetry (1). Similar studies with other systems have further confirmed that quasicrystalline phases do exist with previously forbidden five-fold rotational symmetries (2-5). These structures, however, lack periodic translational order. Figure 1 shows a selected

Figure 1. SADP of an Al-Cu-Ru quasicrystal phase along a five-fold axis.
(Photomicrograph courtesy of J. E. Shield and M. J. Kramer.)

5

area diffraction pattern (SADP) of an Al-Cu-Ru quasicrystalline phase along a five-fold axis. The pentagonal spots illustrate the rotational symmetry, and higher order reflections show the translational aperiodicity. To date, many scientific studies of quasicrystals have been devoted to the interpretation of their atomic structures (6,7). Kelton states that several thousand articles have been published dealing with phase structures of quasicrystals (8). To a far lesser extent, literature exists on the mechanisms of quasi-crystallization and the thermodynamic stability at phase transitions (9).

Recent work has begun to investigate elevated temperature deformation of quasicrystals (5,10). Despite the aggressive research during the past ten years, only a few articles are available describing technical applications and physical properties of quasicrystals. This is likely due to the difficulty in preparing bulk samples of single-phase quasicrystalline materials and the scientific focus of the community initially curious about these fascinating structures.

The characteristic lack of translational symmetry of quasicrystals has generated speculation of attractive physical properties. The atomic structures inhibit normal mechanisms of deformation (e.g., dislocation glide) and result in high hardness at room temperature. Koster reported indentation hardness values from Al-Cu-Fe quasicrystal phases of over 950 kg/mm² (11). While nearly all quasicrystals are brittle at room temperature, there has been some evidence shown of plasticity at higher temperatures; the mechanisms of the deformation, however, has not been fully established. Along with the very high hardness of quasicrystals, some systems possess a relatively high hardness-to-elastic modulus ratio (11). This attribute can be considered as the ability for elastic recovery as well as the incapacity to adsorb impact energy under contact deformation (12). These features describe a low-friction, wear resistant material. It has been further speculated that quasicrystals would be low-friction materials as a result of their atomic structure. This idea rests on the fact that when clean surfaces come into contact with each other, very strong chemical bonding can occur (13). This is particularly true if the mating surfaces have similar crystalline structures so that registry between approaching

electronic distributions occurs (14). The aperiodic atomic arrangement of a quasicrystal should lead to a lack of commensuration between contacting lattices in a clean surface environment, thus reducing the degree of chemical adhesive bonding energy. The net result would again be a low coefficient of friction. In addition to the expected wear resistant behavior of quasicrystals, an unusual behavior has also been discovered; quasicrystals are non-sticking to organic materials, like foods such as eggs. While there is speculation as to why this behavior occurs (15), there is also industrial use of this feature. In the early 1990s, a French newspaper announced the application of quasicrystal surfaces on frying pans (16). One may not necessarily think of cookware as a sophisticated technical application, but it is an excellent use of the capabilities of these unique materials. Other applications ranging from agricultural to automotive uses will likely develop as applied studies of quasicrystals begin to parallel the ongoing fundamental studies.

3.1.2 Composition

Thus far, quasicrystals have been described as a general class of materials. Since the early work which focused on Al-Mn alloys, well over 100 different metallic alloys have been found to form a quasicrystalline phase. Kelton provides a comprehensive review of the subject and describes a large number of different alloy compositions (8). Most alloys do not form a purely quasicrystalline structure; various crystalline phases are usually present. Also, most quasicrystals have been prepared as metastable phases by rapid solidification techniques such as melt-spinning, laser surface melting and low-temperature annealing from an amorphous phase (17). One particular Al-Cu-Fe alloy has been found which forms a thermodynamically stable quasicrystalline phase around an atomic composition of $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ (18). It was shown that this phase was structurally similar before and after annealing for 48 hours at temperatures very close to the phase's melting point.

The thermodynamic stability of the Al-Cu-Fe system and its desirable economic and toxic attributes have caused substantial interest in the characterization and technological development of this particular alloy. One drawback to this system, which has hampered more extensive physical property measurements, is its complex solidification behavior. Gayle (19) performed a study of the Al-Cu-Fe phase diagram around the quasicrystalline (ψ) phase region. His results show that the ψ phase around $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ forms from a liquid-solid reaction involving ternary crystalline phases. Figures 2a and 2b show isothermal sections near the ψ phase at 700°C and 800°C, respectively. At 700°C, it can be seen that three solid phases, λ , β and ω , have equilibrium relationships with the ψ phase.

Upon heating to 800°C, the ω phase reacts with the ψ phase and forms the λ phase and liquid (L). Further heating above 800°C results in the decomposition of the ψ phase into λ and L or λ , β and L. It is likely that the latter reaction occurs since the ψ phase lies within the interior of the $\lambda+\beta+L$ tie triangle.

The above reactions are somewhat easier to visualize by considering the approximate liquidus surface and corresponding reaction scheme offered by Gayle (19), as shown in

Figure 2. Isothermal section of Al-Cu-Fe phase diagram around the ψ phase at (a) 700°C and (b) 800°C (19).

Figure 3. The features of Figure 3 relevant to this study are the reactions at P_1 and the routes taken to arrive at u_2 . The liquidus surface falls along the boundary between the λ and β phases until it reaches P_1 , where the reaction $L+\lambda+\beta \rightarrow \psi$ occurs. Upon further cooling, according to Figure 3a, the liquidus trough can move either between the ψ and λ phases to u_1 , or between the ψ and β phases to u_2 . The former route would involve an additional change in the liquid composition while moving from u_1 to u_2 and necessitate reactions between ω and ψ with liquid to form β . The solidification reactions and products corresponding to the speculated liquidus surface are displayed in Figure 3b. The $Al_{63}Cu_{25}Fe_{12}$ composition used in the proposed study has enough copper to push the liquid composition along the surface between the ψ and β phases; therefore, the liquidus surface moves directly from P_1 to u_2 . Theoretically the liquidus surface would continue along the pathway shown until it finally reaches the eutectic composition identified at E_1 . Analysis of as-cast $Al_{63}Cu_{25}Fe_{12}$ ingots in our

Figure 3. (a) Approximate liquidus surface and (b) suggested reaction scheme for the Al-Cu-Fe system (19).

laboratory suggest that the liquid is consumed prior to reaching the composition of u_2 , i.e., long before reaching E_1 . This is based on identification of phases observed in the as-cast microstructure and the absence of a phase corresponding to the ω structure or composition. These results are discussed in more detail in Chapter 2.

3.1.3 Processing

Like any material, the form in which quasicrystals are used and how they are processed are important considerations. Castings of Al-Cu-Fe are extremely brittle. Fracture toughness measurements obtained from cast ingot sections of $Al_{65}Cu_{20}Fe_{15}$ have produced extremely low values, $\sim 1.5 \text{ MPa}\cdot\text{m}^{1/2}$ (11). As a result of their brittleness, there appears to be a consensus that immediate technological application of quasicrystals in bulk form is unlikely. On the other hand, coatings of these materials are quite promising and have constituted the majority of applied research with Al-Cu-Fe quasicrystals. Coatings have been formed by traditional thermal spraying techniques such as plasma spraying or oxygen-fuel combustion spraying. These coating techniques are used throughout industry to deposit wear resistant coatings such as metallic carbides or oxides (19-21). Plasma spraying, described below, will be used during the proposed research to form coatings for microstructural analysis and tribological characterization.

3.2 Plasma Spraying

Thermal spraying is a common term used to describe a family of coating techniques practiced throughout a wide range of industries. Plasma spraying is one of these techniques and differs from others by the formation of its heat source. The plasma gun dates back to the mid 1950s, when it was introduced for the deposition of alloys and ceramics (22). Since then, equipment improvements, process knowledge, diagnostic techniques and novel coating materials have expanded the applications of plasma spraying. Materials for modern high

performance machinery are commonly subjected to extreme temperatures and mechanical stresses beyond the materials' inherent capabilities. It is becoming increasingly common to form coatings on machinery surfaces to protect against high temperature corrosive media and to enhance mechanical wear and erosion resistance. Several thousand parts within an aircraft gas turbine engine have protective coatings, many of them plasma sprayed. In fact, plasma spraying has emerged as a major means to apply a wide range of materials on diverse substrates. The process can be readily carried out in air or in environmental chambers and requires very little surface preparation. The rate of deposit buildup is rapid compared to vapor phase deposition processes, and the costs are comparatively low.

The plasma gun is composed of an anode, acting as a front nozzle, and a tungsten cathode. Figure 4 shows a schematic representation of a typical plasma gun. The plasma is initiated by a high frequency pulse to form an arc between the electrodes. The arc is stabilized and maintained under a high current, low voltage input by the continuous flow of new arc gas which is fed into the plasma gun. The development of the electric arc in the presence of a gas

Figure 4. Schematic drawing of cross section of a plasma spray gun.

between positive and negative electrodes gives rise to a breakdown of the dielectric nature of the gas. Electrons and ions are formed, which are accelerated toward the positive and negative electrodes, respectively. These rapidly moving particles collide with neutral atoms and molecules, creating further ionization and, thus, an avalanche effect. The net result is a gaseous collection of energetic electrons and ionized molecules—a plasma (23).

Arc gases are primarily argon or nitrogen, although hydrogen is often added to increase the enthalpy of the plasma due to the energetics of the dissociation of diatomic hydrogen. Temperatures within the core of a plasma can reach 15,000 K, but the temperature falls off rapidly, both radially from the core and axially away from the cathode (24). Nevertheless, the extreme temperatures generated in plasma guns provide sufficient energy to melt any material which has some form of a liquid phase. Very refractory carbides such as TiC or HfC, which melt near 4000°C, are routinely processed into dense coatings by this process.

The plasma exits from the gun, as indicated in Figure 4, as a high velocity flame. The flame temperature distribution decreases significantly both radially, outward from the plasma center, and down the axis from the anode outer face. The desired coating material begins in a powder form, which is fed into the plasma in a stream of a carrier gas. The powder can be introduced into the plasma internally within the gun, as depicted in Figure 4, or externally into a cooler region of the plasma. The injected powder accelerates, melts fully or partially, and is carried away at high velocities to the substrate on which the particles impact, rapidly solidify at cooling rates that can approach about 10^{-6} K s^{-1} and form a thick, tenaciously bonded coating (25).

In this complex process of particle melting, accelerating and rapidly solidifying, more than 50 interrelated processing parameters can determine particle temperature and velocity and thus, influence the quality of the coatings obtained (25). Of these parameters, many are independent and must be optimized empirically in order to achieve an acceptable coating.

Figure 5 identifies some of the parameters which will play important roles in the plasma spray process.

Undoubtedly, one of the most critical factors in forming plasma sprayed coatings is the feedstock powder. Ideal feedstock powder particles would be spherical, dense, chemically homogeneous and free flowing. There are many techniques used to prepare feedstock powder for plasma spraying (e.g., gas or water atomization or casting and crushing). Gas atomization typically produces a powder with spherical morphology with good homogeneity due to high cooling rates. However, atomization techniques are often impractical with high melting temperature materials because of problems with containing the material in a superheated state. Powder synthesis by casting and crushing involves pulverizing a cast ingot into a powder followed by screening to a desired size distribution. While this method is applicable to very refractory materials (e.g., metal carbides), cooling rates are relatively low even in chilled metal molds, particularly in large castings. The slow cooling can cause excessive segregation in the starting cast microstructure, depending on the material. The inhomogeneity caused by the

Figure 5. Plasma spraying parameters which affect coating microstructure and properties (26).

solidification segregation is carried over to the powder and ultimately to the coating. In addition to differences in chemical uniformity, the particle morphology developed by the above processes are quite contrasting. As stated earlier, the gas atomized powders are generally spherical, while cast and crushed powder is blocky and irregular. These morphological features affect the flowability of the powder. Poor flow characteristics result in difficulties in plasma spraying uniform, dense coatings.

4. Summary

Our lab has been working with plasma spraying of both high pressure gas atomized (HPGA) and cast and crushed quasicrystal powders. A major component of this research includes comparative studies of PAS coatings formed with starting powders prepared by both techniques. In addition, a thorough investigation of the effects of starting powder particle size on coating microstructure is included. During the course of the overall research, an interest developed in forming Al-Cu-Fe materials with finer grain sizes. Therefore, a brief study was performed to characterize the effect of adding boron to Al-Cu-Fe materials prepared by different techniques. In addition to characterizing the microstructural features of the above materials, oxidation and wear behavior was also examined.

References

1. D. Shechtman, I. Blech, D. Gratias and J. W. Cahn, Phys. Rev. Lett. 53, 1951 (1984).
2. J. Tartas and E. J. Knystautus, J. Mater. Res. 6, 1219 (1991).
3. G. Gozlan, C. Bergen, G. Fourcaudot, R. Omari, J. C. Lasjavnias and J. J. Prejaean, Phys. Rev. Lett. 44, 101 (1991).

4. P. Sainfort and D. Dubost, *Quasicrystalline Materials*, edited by C. Janot and J. M. Dubois (World Scientific, Singapore, 1988) p. 361.
5. S. S. Kang and J. M. Dubois, *Phil. Mag.* **A65**, 151 (1992).
6. A. I. Goldman and M. Widom, *Annu. Rev. Phys. Chem.* **42**, 685 (1991).
7. P. J. Steinhart and D. P. DiVincenzo, *Quasicrystals: The State of the Art* (World Scientific, Singapore, 1991).
8. K. F. Kelton, *Int. Mater. Rev.* **38**, 105 (1993).
9. W. Liu and U. Köster, *Proceedings of Seventh International Conference on Rapidly Quenched Materials*, RQ7, Sweden, (1990) p.13.
10. J. E. Shield, M. J. Kramer and R. W. McCallum, *J. Mater. Res.* **8**, 1199 (1993).
11. U. Köster, W. Liu, H. Liebertz and M. Michel, *J. Non-Crystal. Sol.* **153 & 154**, 446 (1993).
12. B. R. Lawn and V. R. Howes, *J. Mater. Sci.* **16**, 2745 (1981).
13. I. M. Hutchings, *Tribology* (CRC Press, London, 1992) p. 77.
14. J. Ferrante and J. R. Smith, *Surf. Sci.* **38**, 17 (1973).
15. R. Rivier, *J. Non-Crystal. Sol.* **153 & 154**, 458 (1993).
16. *Gazette de Lausanne*, (19 April 1990) p.11.
17. A. P. Tsai, A. Inoue and T. Masumoto, *Jap. J. Appl. Phys.* **26**, L1505 (1987).
18. A. P. Tsai, A. Inoue and T. Musomoto, *J. Mater. Sci. Lett.* **7**, 322 (1988).
19. F. W. Gayle, A. J. Shapiro, F. S. Biancaniello and W. J. Boettinger, *Met. Trans. A* **23A**, 2409 (1992).
20. C. d'Angelo and H. El Joodi, *Adv. Mater. Process.* **41**, 39 (1988).
21. M. E. Vinayo, F. Kassabji, J. Guyonnet and P. Fauchais, *J. Vac. Sci. Technol.* **A3**, 2483 (1985).
22. H. L. Filmer, J. Hochstrasser and A. R. Nicoll, *Ceram. Bull.* **69**, 1955 (1990).
23. M. L. Thorpe, *Adv. Mater. Process.* **144**, 50 (1993).

24. D. A. Frank-Kamenetskii, *Plasma* (MacMillan, New York, 1972) p. 18.
25. H. Herman, *Sci. Am.* **258**, 112 (1988).
26. J. H. Zaat, *Am. Rev. Mater. Sci.* **13**, 9 (1983).
27. J. E. Shield, A. I. Goldman, I. E. Anderson, T. W. Ellis, R. W. McCallum and D. J. Sordelet, U. S. Patent Application, ISURF #I01474.
28. S. S. Kang and J. M. Dubois, *J. Mater. Res.* **8**, 2471 (1993).
29. J. M. Dubois, S. S. Kang and J. Von Stebut, *J. Mater. Sci. Lett.* **10**, 537 (1991).
30. E Hornbogen and M. Schandl, *Z. Metallkd.* **83**, 129 (1992).
31. P. J. Blau, Oak Ridge National Laboratory, private communication.

CHAPTER 2:
EFFECT OF STARTING POWDERS ON CONTROLLING MICROSTRUCTURAL
DEVELOPMENT OF Al-Cu-Fe QUASICRYSTALLINE PLASMA SPRAYED COATINGS

A paper accepted by the *Journal of Thermal Spray Technology*

D. J. Sordélet, M. J. Kramer, and O. Unal

Ames Laboratory, U. S. DOE, Iowa State University
Ames, IA 50011

Abstract

Powders and plasma sprayed coatings of an $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy containing a quasicrystalline phase were characterized by x-ray diffraction, electron microscopy and differential thermal analysis. The relationships between powder and coating microstructures were examined. Powders were produced by (i) casting and crushing and (ii) by gas atomization. Both techniques produced powders with multiple phases; cubic and monoclinic ternary structures were formed along with the face-centered icosahedral quasicrystalline phase. These phases were also produced in the plasma arc sprayed coatings formed using the different starting powders. Cooling rates during powder processing greatly affected the phase equilibria and scale of segregation of this alloy. Finer grain sizes in the plasma sprayed coatings were obtained from the more chemically homogeneous gas atomized powders.

[Key words: plasma spraying, Al-Cu-Fe alloys, quasicrystals]

1. Introduction

Quasicrystals have five-fold rotational symmetries, which were previously forbidden by classical laws of crystallography, but do not exhibit long-range periodic translational order. Over 100 alloy systems have been identified to contain a quasicrystalline phase. This new class of materials, fitting somewhere between amorphous and crystalline materials, has many fascinating properties. Quasicrystals formed in the Al-Cu-Fe system are among the few alloys which have had several of their physical properties, e.g., hardness, thermal expansion and thermal conductivity, studied. Al-Cu-Fe quasicrystals have low density ($4\text{-}5\text{ g/cm}^3$), high hardness, ($600\text{-}1000\text{ kg/mm}^2$) and a high elastic modulus ($70\text{-}100\text{ GPa}$) (1). The high hardness, together with high elastic moduli, indicates a good ability for elastic recovery as well as the capacity to absorb impact energy under contact deformation (1). Previous studies have also shown that Al-Cu-Fe quasicrystalline alloys have favorable wear-resistant and low friction properties, but the performance of these coatings is compromised by a coarse, heterogeneous microstructure (2,3). The objective of the current study is to compare the chemical uniformity and the microstructure of starting powders produced by different techniques to characteristics of the resulting plasma sprayed coatings in an attempt to produce a finer, more homogeneous microstructure.

The microstructures and properties of thermal spray coatings can be altered by varying the preparation techniques of the feedstock powders. The chemical uniformity and morphology of powders are well known to strongly impact the physical and chemical properties of thermal spray coatings. Kubel (4) reviewed a variety of powder manufacturing methods and focused on the impact of chemical uniformity and particulate morphology on Ni-Al coating characteristics. Other studies have consistently demonstrated that very fine-scale chemical uniformity and spherical powder morphology produce improved coating properties (5-7). For example, oxidation or corrosion rates may be accelerated due to phase segregation in the alloy coating, especially if chemical inhomogeneities produce localized anodic and

cathodic sites (8). Mechanical properties, e.g., wear resistance or thermal cycling fatigue resistance, may be compromised by lower coating densities induced by poor powder morphologies.

Processing of feedstock powder may involve solidification, e.g., atomization or ingot casting followed by crushing, or solid state reactions, e.g., spray drying followed by sintering. In the atomization processes, a superheated melt stream is disintegrated and rapidly solidified using water or gas jets resulting in a Gaussian distribution of powder sizes. Morphologies of atomized powder range from primarily spherical for gas atomized to irregular for water atomized. The very high cooling rates of atomization processes tend to produce high chemical uniformity for alloyed systems. Casting of materials followed by crushing into powder is frequently used to produce powders of ceramics and brittle metal alloys which are not readily produced by atomization processes. Casting and crushing of alloys suffers from large-scale chemical segregation due to low cooling rates; furthermore, powder morphologies developed through crushing are typically angular and very irregular.

2. Experimental Procedures

2.1 Starting Powders

A starting composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ was used throughout this study. This composition falls within the quasicrystalline (ψ) single-phase region of the phase diagrams determined by Gayle et al. (9) and Gratias et al. (10). For the casting and crushing method, a five kilogram ingot was prepared by induction melting a mixture of Al (99.999), Cu (99.99) and Fe (99.99) in an alumina crucible under an argon atmosphere. The melt was heated to 1100°C and held for 15 minutes before being bottom poured into a water-chilled 5 cm diameter by 50 cm long copper mold. The cast ingot was subsequently fractured into smaller pieces and then ground in a motorized agate mortar and pestle. The ground powder was air classified into a distribution between 5 and 45 μm for plasma spraying. Prior to fracturing the cast ingot, a

1 mm thick wafer was cut from the midsection of the ingot for characterization of the as-cast microstructure.

The second powder was prepared by a gas atomization technique. Similar starting material purities were employed. Following powder synthesis, the powder was air classified to yield a +5, -45 μm size distribution. The two powder processing techniques employed in this study allowed examination of two extremes in solidification rates. Throughout the following text, the symbols (CC) and (GA) will refer to the cast and crushed powder and the rapidly solidified gas atomized powder, respectively.

2.2. Plasma Spraying Process

Air plasma spraying was performed using a Miller Thermal SG-100 gun. Mild steel substrates were degreased and grit blasted with 24-grit Al_2O_3 . Two coating thicknesses of each powder were prepared, $\sim 200\ \mu\text{m}$ and $\sim 800\ \mu\text{m}$, to assess coating microstructure effects related to differences in cooling rates of the coatings. Plasma spraying parameters were briefly evaluated to achieve reasonably dense microstructures (Table 1). These conditions were used with both the CC and GA powders.

Metallographic samples of the plasma sprayed coatings were prepared by mounting a cut section of the coated steel substrate in epoxy and sectioning with a low speed diamond saw. The blade entered the coating and exited through the back of the substrate to help prevent spallation. Grinding and polishing was performed on an automatic system using an initial 180-grit SiC paper followed by 9 and 3 μm diamond lapping. A final polish with 0.05 μm Al_2O_3 was employed to remove scratches, particularly in the substrate.

Table 1. Plasma spray parameters used for cast and crushed and gas atomized $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders.

Gun	Miller Thermal SG-100
Anode	2083-358 (Mach I mode)
Cathode	112
Gas injection	113
Current, amperes	800
Voltage, volts (@ gun)	43.6
Arc gas (Ar) flow rate, slpm	37.8
Auxiliary gas (He) flow rate, slpm	20.0
Powder carrier gas (Ar) flow rate, slpm	5.6
Powder feed rate, g/min	20.0
Spray distance, cm	7.5
Powder size, μm	+5, -45

2.3 Characterization Techniques

The compositions of the starting powders and plasma sprayed coatings, after removal from the substrates, were measured by the inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) technique. Oxygen contents of the same materials were determined by inert gas fusion.

The composition of the phases formed in the cast ingot were determined using an ARL SEMQ electron microprobe. Standard samples of high purity Al, Cu and Fe were prepared by the Materials Preparation Center of the Ames Laboratory for standardization of background spectra used in the electron microprobe (EMP) analysis. At least twenty measurements were taken of each phase in the bulk sample cut from the ingot midsection.

X-ray diffraction (XRD) was performed with a Philips 1810 diffractometer using $\text{CuK}\alpha$ radiation to qualitatively characterize the phases in the cast ingot, starting powders and plasma sprayed coatings. The cast ingot section and starting powders were x-rayed in their existing form, while the plasma sprayed coatings were ground to eliminate any texturing effects.

The as-solidified microstructures of the cast ingot, GA powder and plasma sprayed coatings were observed with a JOEL 6100 scanning electron microscope (SEM) and a Philips CM30 transmission electron microscope (TEM).

For planar sections of the plasma sprayed coatings, 3 mm disks were electro-spark-cut from the coated substrates and mechanically ground and polished from the substrate side to $\sim 50\ \mu\text{m}$ thick with the result that only the near top surface of the coating was investigated. For cross-sections, two small pieces of coating were epoxied face-to-face and mechanically thinned to $50\ \mu\text{m}$. Ion-milling to perforation was performed at 3 kV using a liquid nitrogen-cooled stage to minimize milling damage.

Differential thermal analysis (DTA) was performed to compare the thermal events on heating of the CC and GA powders as well as the plasma sprayed coatings prepared from the two powders. The DTA results were obtained with a Perkin Elmer System 7 unit. Scans were performed in flowing argon using a heating rate of $10^\circ\text{C}/\text{min}$. and approximately 50 mg samples of ground powder.

3. Results

3.1 Cast Ingot

The solidification microstructure of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ ingot is displayed in Figure 1. Three phases are clearly visible. The dark phase exhibiting a dendritic morphology appears to have solidified first followed by the medium gray phases surrounding the dendrites. Finally, the light gray phase appears to have formed from the final interdendritic liquid. The contrasting

Figure 1. SEM micrographs (secondary electrons) of polished cross sections of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ cast ingot. (a) Is from outer rim region of ingot. (b) Is from center region of ingot.

(a)

(b)

cooling rates between the inner and outer regions of the cast ingot are manifested in the resulting scale of segregation; the microstructure of the inner ingot region is characterized by larger grains than the outer region, which cooled more rapidly due to the chilling of the water-cooled copper mold wall. The two regions appear to differ only in grain size, not in the number or composition of phases. This was confirmed by EMP and structural analysis, as discussed later.

Figure 2 illustrates the phases in the cast ingot section identified with XRD. The diffraction patterns were determined to contain four phases: face-centered icosahedral $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ (ψ), monoclinic $\text{Al}_{13}\text{Fe}_4$ (λ), cubic AlFe (β) and tetragonal Al_2Cu (θ). The latter three phases are isostructural with these stoichiometric compounds. However, as discussed

Figure 2. X-ray diffraction pattern of bulk specimen cut from $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ cast ingot.

later, these phases were found to be ternary compounds. The monoclinic, cubic and tetragonal phases have the $C2/m$, $Pm\bar{3}m$ and $I4/mcm$ space groups, respectively. The peaks originating from the quasicrystalline phase (ψ) are associated with the face-centered icosahedral structure. These results are in agreement with the work of Gayle et al. (9). According to the isothermal sections of the Al-Cu-Fe phase diagram proposed by Gayle, the $Al_{63}Cu_{25}Fe_{12}$ composition does not melt congruently and should reside in a single-phase face-centered icosahedral region. Clearly, equilibrium was not achieved in the cast ingot, nor would one expect it to be under these conditions. The presence of the θ phase was not observed in the SEM micrographs or detected with EMP. This phase is the lowest melting phase present. Therefore, it is likely to be uniformly distributed throughout the very fine interdendritic regions. In addition, the θ phase is chemically similar with β , making detection more difficult, particularly in a secondary electron image.

The approximate compositions of the phases shown in Figure 1 were determined by EMP analysis. The results are displayed in Table 2 along with the phases' corresponding crystal structures. The description of phases based on gray scales refers to the SEM micrographs displayed in Figure 1. Grains from the inner and outer ingot section were analyzed, but no significant compositional differences were observed as long as sufficiently large grains were selected.

Table 2. Characterization results of $Al_{63}Cu_{25}Fe_{12}$ cast ingot.

<u>Phase region</u>	<u>Symbol Designation</u>	<u>Composition</u>	<u>Crystal Structures</u>
Medium gray	ψ	$Al_{64}Cu_{24}Fe_{12}$	Face-center icosahedral
Dark gray	λ	$Al_{72}Cu_5Fe_{23}$	Monoclinic
Light gray	β	$Al_{55}Cu_{40}Fe_5$	Cubic

A sample from the cast ingot section was observed in TEM. Figure 3a, b and c show TEM micrographs corresponding to the ψ , λ and β phases, respectively. A two-fold diffraction pattern for the ψ phase, $[110]$ pattern for the λ phase and $[111]$ pattern for the β phase are included as insets to the micrographs. It is clear from the micrographs in Figure 3 that the three phases have distinctive morphological features. Quasicrystal grains in general do not have any defects or bend contours, indicating that it is brittle and dislocation activity is not favored. On the other hand, intermetallic phases of λ , which twins on the (001) planes, and β contain distinct planar defects and dislocations, respectively. Identification of phases was made by a systematic study of electron diffraction patterns. Energy dispersive spectroscopic (EDS) studies were also made, but although the findings were generally in agreement with the EMP findings presented above, EDS was inconclusive for identification purposes due to the large solubility of Cu in AlFe. Unequivocal identification of the crystal structure and chemistry of specific grains, seen in Figure 1, was therefore made by comparing the results of electron diffraction, XRD, and EMP studies. The composition of the ψ phase is very close to the starting composition, $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$. The λ phase has an approximate stoichiometry of $\text{Al}_{13}\text{Fe}_4$. On the other hand, the β phase is far from the AlFe composition. Gayle et al. reported that this structure has a large solubility for Cu (9). Their results with varying compositions confirmed that up to 45% Cu can be accommodated by the β structure along with Fe and Al. The Cu substitution observed in β results in an increase in the lattice parameter by $\sim 1.1\%$.

3.2 Starting Powder

The microstructure of the CC powder is very similar to the microstructure of the starting ingot (Fig. 1). Figure 4a shows the distribution of phases throughout the crushed particles. The cross sectional microstructure of the GA powder is presented in Figure 4. The effects of the high cooling rates operative in preparing the GA powder are clearly visible.

Figure 3. Bright field TEM micrographs of selected grains in bulk specimen cut from $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ cast ingot. (a) Corresponds to the medium gray phase in Figure 1. This is the ψ phase showing few defects. The SADP insert is for a two-fold zone axis showing rotational but lacking translational symmetry; (b) Corresponds to the medium dark gray phase in Figure 1. This is the λ phase which is characterized by numerous twin lamellae. The SADP insert is for a $[110]$ zone axis projection. (c) Corresponds to the light gray phase in Figure 1. This is the β phase showing numerous defects. The SADP insert is for a $[111]$ zone axis projection.

(a)

(b)

(c)

Figure 4. SEM micrograph (backscattered electrons) from polished cross sections of (a) gas atomized (GA) powder particle and (b) cast and crushed (CC) particles.

(a)

(b)

There is still some segregation present in the GA powder, but the scale is much less than the CC powder and precluded chemical analysis by traditional EMP.

The phases detected in the CC and GA powders by XRD are shown in Figure 5. Comparing the trace from the CC powder in Figure 5 to the trace obtained from the cast ingot bulk section in Figure 2 reveals two interesting differences. First, the powder sample shows more of the θ phase. Second, the relative intensities of the θ and λ phases are quite different. The first difference is likely due to sampling differences. The cast ingot bulk section, which was cut prior to crushing and grinding, represents a very small percentage (<1%) of the entire ingot. Conversely, the powder sample is much more likely to represent all the phases present in the ingot. With the large-scale segregation exhibited by the peritectic forming phases, it is

Figure 5. X-ray diffraction pattern of (a) cast and crushed (CC) powders and (b) gas atomized (GA) powders.

likely that the small cast ingot bulk section had an uncharacteristically small fraction of the θ phase. The discrepancies between the relative intensities of the θ and λ phases are most likely the result of texturing in the cast ingot bulk specimen. The low symmetries of the tetragonal θ and monoclinic λ typically produce preferred orientation in slower cooling rate solidification methods.

The GA powders show two primary phases: β and ψ . Also, the GA powders qualitatively appear to have a higher ψ phase content than the CC powder. However, this judgment by comparing peak heights is very suspect, particularly considering the complex atomic structure and scattering phenomena associated with the quasicrystalline ψ phase.

3.3 Plasma Sprayed Coatings

Plasma spraying parameters were adjusted to produce relatively dense-appearing coatings. Individual splats were analyzed to observe the melting and projection behavior of the CC and GA powders. Figures 6a and 6b show typical splat morphology produced with the GA and CC powders, respectively, using the parameters described in Table 1. The extremely fine grain structure of the CC splat after removal from the substrate is seen in the TEM micrograph in Figure 6c. The coating micrographs in later figures will demonstrate the substantial grain coarsening which occurs during plasma spray deposition.

Chemical analysis of the CC and GA powders and plasma sprayed coatings are presented in Table 3. The nominal composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ is retained by the powders, but the coatings have shifted away from the initial composition. The splats in Figure 6a and 6b are indicative of a very well-melted particle; selective vaporization of Al may have caused the deviation in the composition of the coating. Oxygen levels for the CC and GA powders are comparable. During plasma spraying, some oxidation occurs with roughly one order of

Figure 6. (a) SEM micrograph (secondary electrons) of an individual splat of gas atomized (CC) powder particle and (b) Bright field TEM image from center area of splat shown in (a). The insert is a SADP of this area which indexes to a simple cubic structure with $a_0 = 0.41$ nm.

(a)

(b)

Table 3. Chemical analysis of cast and crushed and gas atomized powders and plasma sprayed coatings.

<u>Sample</u>	<u>Al(a/o)</u>	<u>Cu(a/o)</u>	<u>Fe(a/o)</u>	<u>O(ppm by weight)</u>
CC starting powder	63.5	24.8	11.7	591
GA starting powder	64.3	25.0	10.7	438
Thin coating, CC powder	61.7	26.1	12.1	7844
Thick coating, CC powder	60.6	27.1	12.3	
Thin coating, GA powder	62.3	26.0	11.8	9544
Thick coating, GA powder	60.9	26.6	12.5	

magnitude increase in oxygen. These levels are far too low to detect by XRD. Distinct oxide particles were not detected in TEM; however, the oxygen is probably present as a metallic oxide surface film on prior splat boundaries rather than as an interstitial solution or a precipitated oxide phase.

Polished cross sections of coatings formed with CC and GA powders are shown in Figure 7. The coarse inhomogeneity observed in the cast ingot is retained in the CC powder coating (Fig. 1). The GA powder coatings exhibit far less chemical segregation. While the benefits to chemical uniformity of the GA powders are clearly visible in Figure 7, the expected differences in porosity and fractions of unmelted or partially melted particles using the irregular, angular CC powder and the more desirable spherical morphology of the GA powder were not observed. Additional work is needed to tailor the plasma spraying parameters for this composition and particle size to produce denser coatings.

X-ray diffraction patterns obtained from plasma sprayed coatings prepared with the two different powders are shown in Figure 8. The patterns shown were obtained from the thick coatings; however, the patterns from thin CC and GA powder coatings were nearly identical.

Figure 7. SEM micrographs (backscattered electrons) of polished cross sections of plasma sprayed coatings formed with (a) cast and crushed (CC) powders and (b) gas atomized (GA) powders.

(a)

(b)

The quasicrystalline ψ and crystalline β phases are clearly visible in both coatings. The CC powder coating does not show any reflections from the θ phase present in the starting powder (Fig. 5). The λ phase is not easily identified in Figure 8. As discussed earlier, this latter observation may be due to the similar d-spacings of the highest intensity peaks corresponding to the ψ , β and λ phases.

Figure 8. X-ray diffraction of plasma sprayed coatings formed with (a) cast and crushed (CC) powder and (b) gas atomized (GA) powders.

Bright field imaging and electron diffraction of the plasma sprayed coatings provided an interesting complement to the bulk XRD information discussed above. Figure 9 displays several representative TEM micrographs obtained from CC and GA powder coatings. Note that images from the GA coating are shown in both a planar section, i.e., normal to spray direction, and a cross sectional view, i.e., parallel to spray direction. Figure 9a shows that in the CC coating, the crystalline phases, in particular λ , have a grain size in excess of $1\ \mu\text{m}$. The ψ phase grain size generally tends to be $< 1\ \mu\text{m}$. This is well demonstrated by the selected area diffraction pattern (SADP) in which a continuous ring pattern is observed for the ψ phase while only a single off-zone axis pattern, which indexes to the λ phase, is observed when using a $10\ \mu\text{m}$ aperture (Fig. 9a insert). The λ phase in Figure 9a has an identical structure to that shown in Figure 3b. For the GA coatings, all grains tend to be sub-micron (Fig. 9b). Analysis by TEM/EDS reveals that the λ and ψ grains have nearly the same composition as those determined by EMP for the as-cast ingot. The compositions determined by EDS from the TEM specimens are displayed in Table 4. The β phase was not observed in EDS in this region, but diffraction spots were identified, as seen in the insert in Figure 9b. Careful analysis of an electron diffraction pattern obtained from broad areas, i.e., 50 to $100\ \mu\text{m}$, demonstrated that the β phase does indeed occur in the plasma sprayed coatings, as also seen in XRD (Fig. 8b).

Table 4. EDS data taken at the numbered spots shown in Figure 9b. Spots 1, 3 and 4 closely correspond to the (λ) phase, while spots 2 and 5 correspond to the (ψ) phase.

Spot Number	Al(a/o)	Cu(a/o)	Fe(a/o)
1	73.9	7.0	19.2
2	62.9	23.4	13.7
3	72.7	8.1	19.2
4	75.1	6.7	18.3
5	68.4	20.4	11.2

Figure 9. Bright field TEM micrographs of plasma sprayed coatings. Starting powders and orientation are as follow: (a) cast and crushed (CC) powder, planar section showing a large λ grain (arrowed) and corresponding diffraction pattern (arrowed on insert); (b) gas atomized (GA) powder, planar section showing a much finer grain size distribution for the crystalline phases. The numbered grains correspond to EDS points displayed in Table 4; and (c) gas atomized powder, cross-section showing the amorphous Al-rich region (arrowed) in between the fine polycrystalline regions. Insert is a SADP showing ψ , β and λ phases.

(a)

(b)

(c)

Figure 9c shows a typical cross-section of the GA coating. The only obvious difference in the cross-sections compared to the planar views are the narrow Al-rich regions (~10 nm wide) between poly-phased sections up to 2 μm across. Although these regions were amorphous, it is not known if they represent elemental Al or an oxide phase since the EDS detector used has a thick Be window and cannot detect O. The size and approximate cross-sectional area of these regions are consistent with the expected size of a single splat so the Al-rich regions may be the boundary area between individual splats. Although not specifically analyzed in this study, the Al-rich areas may be splat surface oxides formed during spraying. Estimation of the oxygen contribution of a 10 nm thick Al_2O_3 skin which forms on a splat produced from a 25 μm diameter sphere is within one order of magnitude of the oxygen levels measured from the plasma sprayed coatings.

Due to the numerous overlapping peaks and different X-ray scattering factors for the various phases seen in the XRD and SADP data, DTA was used in an attempt to provide a more sensitive indication of the presence of minor phases and their relative proportions. Figure 10 illustrates the DTA traces for the CC and GA powders. It is readily seen that the CC powder has more endothermic transitions with stronger signatures than the GA powder. The first strong endothermic reaction near 600°C appears to be the peritectic decomposition of the θ phase to liquid and a tetragonal $\text{Al}_7\text{Cu}_2\text{Fe}$ (ω) phase (11). The ω phase decomposes around 710°C and is followed by melting of the ψ phase near 840°C. Since the ω phase is a transient phase, it did not show up in the XRD patterns of the CC powder. Curve "b" on Figure 10 shows only a slight indication of the above reactions for the GA powders, confirming the increased homogeneity of these powders. After plasma spraying, both the CC and GA coatings exhibited fewer low temperature thermal events compared to the starting powders, as shown in Figure 11. Both the CC powder thick and thin coatings have a small amount of ω decomposition which is not observed in the GA powder coatings. The onset of melting near 900°C is nearly constant for all the coatings, which indicates that the composition of the ψ

Figure 10. DTA thermogram obtained on heating (a) cast and crushed (CC) powder and (b) gas atomized (GA) powder. The endothermic reactions are discussed in the text.

Figure 11. DTA thermogram obtained on heating of (a) cast and crushed (CC) thin coating; (b) gas atomized (GA) thin coating; (c) cast and crushed thick coating; (d) gas atomized thick coating. All show the same melting temperature of the ψ phase, but different high temperature behavior.

phase is consistent from coating to coating. The behavior above the onset of melting is different for the CC and GA materials, showing that the proportion of the high temperature phases, λ and β , is different, contrary to Figure 8.

4. Discussion

The contrasting cooling rates experienced by the CC and GA powders produced significantly different solidification microstructures for this Al-Cu-Fe alloy. The degree of chemical segregation is the most visible difference, but this would be expected with the peritectic reactions which are characteristic to the Al-Cu-Fe system. Apparently, even the rapid solidification history of the atomized powders was not able to bypass the peritectic reaction and its resulting segregation. The structures of the phases formed in the two powders are similar, although the slower cooling of the original ingot from which the CC powder was formed provided the opportunity to form the lower melting temperature θ phase. The macro-inhomogeneities developed in the chill cast ingot of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ composition are seen in comparing Figures 1 and 5. It is straightforward to recognize that individual particles produced by crushing the cast ingot into a 5-45 μm particle size distribution can have completely different chemical compositions and crystalline structures. These inhomogeneities are clearly demonstrated in the SEM micrographs (Fig. 1) and DTA traces (Fig. 10). The differences in chemical homogeneity between the CC and GA powders are retained in coatings formed from the two powders.

The DTA analyses are more indicative of the relative fractions of the various phases. Curve "b" in Figure 10 shows only a slight indication of reactions from the θ and ω phases for the GA powders, which confirms that the majority of the material is comprised of the ψ and β phases. The apparent significance of the prominent β peak in the XRD pattern shown in Figure 5b is due to structure factor considerations. The β phase is body-centered cubic and, therefore, has only a few strong scattering planes. Conversely, the ψ and λ phases have numerous planes

which have small scattering factors. Therefore, direct correlation of phase content based on peak areas or intensities can be misleading. Based on the above observations, it appears that the GA powders have higher fractions of the ψ and β phases than the CC powders and coatings. However, these differences are not as pronounced in the plasma sprayed coatings.

Comparison of the XRD traces obtained from sprayed coatings and TEM micrographs reveals an apparent anomaly. The XRD results in Figure 8 indicate the presence of two phases: ψ and β . However, the bright field TEM images in Figure 9 show that the monoclinic λ phase is present in both the CC and GA powder coatings. It is quite possible that this result is due to chemical variations of the individual phases, in particular the λ and β phases. The strongest reflections for the ψ , β and λ structures are centered around a close range of two-theta values between 44 and 46°. Extensive substitutional solid solution could make resolution of individual planar reflections very difficult, depending upon peak shifting. Evidence of variable phase compositions is also indicated by the data shown by curve "a" in Figure 8. The peaks appear to have broadened in the CC powder coating. Typically this effect would be due to small grain sizes, i.e., $<1\ \mu\text{m}$. However, the apparent grain size, particularly in the crystalline phases, was too large to create this effect. Compositional variations could produce the integrated peak shifting seen in the XRD scan. This effect would make the resolution of ψ , β and λ peaks even more difficult if the phases exhibiting substitutional solid solution were present in a range of stoichiometries. Subtle peak shifts from these deviations in phase chemistries could bring adjacent peaks even closer together.

Thus far, attention has been focused on the differences between the CC and GA powders and the coatings obtained from them. The GA powders are clearly more homogeneous than the CC powders; however, they still result in a multi-phase coating. The individual splat shown in Figure 6 helps illustrate the barrier to directly forming a single-phase structure with the Al-Cu-Fe system. The very fine grain structure is a precursor for the larger grains which form during plasma spraying. The particular CC splat analyzed has a metastable

structure. The cubic structure of the splat is similar to the β phase observed in the powders and coatings, but it appears to be highly disordered. It could not be indexed to a body-centered cubic lattice. Since the splat was formed from the CC powder, it is possible that the individual particle which formed the splat was rich with the β phase. Nevertheless, the disordered structure still must evolve to the structure seen in the plasma sprayed coatings. This evolution is likely a solid state diffusion phenomenon. The heat provided by incoming molten particles together with the heat liberated during solidification provides the energy to activate the microstructural development. If the splat solidification process is indeed characteristic of the Al-Cu-Fe system, which has a very complex solidification path, then it would be desirable to produce powder having an even finer degree of chemical homogeneity than seen with GA powders examined in this study.

5. Conclusion

The complex phase equilibrium relationships of the Al-Cu-Fe system makes powder synthesis by solidification processes strongly dependent upon cooling rates. Casting and crushing an $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy ingot produced very large-scale phase separation as compared to a rapid solidification technique. Solidification of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ composition yields a multi-phase alloy which contains a quasicrystalline phase very close to the starting composition and several ternary intermetallic phases. The powder solidification microstructure characteristics were clearly reflected in the final plasma sprayed coating microstructures. Cast and crushed powder yielded chemically inhomogeneous coatings with large ($>1\ \mu\text{m}$) grain sizes. On the other hand, rapidly solidified powder produced more chemically uniform coatings with much finer grain sizes.

Acknowledgments

The authors would like to thank L. P. Lincoln and M. F. Besser for the technical expertise in preparing the ingot castings and performing the plasma spraying, respectively. The efforts of I. E. Anderson and R. Terpstra in synthesizing the rapidly solidified powder are acknowledged. This study was performed at the Ames Laboratory, Iowa State University and was supported by the director of Energy Research, Office of Basic Sciences, United States Department of Energy under contract No. W-7405-ENG-82.

References

1. U. Köster, W. Liu, H. Leibertz, and M. Michel, Mechanical Properties of Quasicrystalline and Crystalline Phases in Al-Cu-Fe Alloys, *J. Non-Crystall. Solids*, Vol 153 & 154, 1993, p 446-452.
2. J. M. Dubois, S. S. Kang and J. Von Stebut, Quasicrystalline Low-Friction Coatings, *J. Mater. Sci.*, Vol 10, 1991, p 537-541.
3. S. S. Kang, J. M. DuBois, and J. Von Stebut, Tribological Properties of Quasicrystalline Coatings, *J. Mater. Res.*, Vol 8, No. 10, 1993, p 2471-2481.
4. E. Kubel, Jr., Powders Dictate Thermal Spray Coating Properties, *Adv. Mater. Proc.*, Vol 138, 1990, p 24-26.
5. D. L. Houck, Techniques for the Production of Flame and Plasma Spray Powders, *Modern Developments in Powder Metallurgy*, Vol 12, 13, and 14, 1980, p 485-504.
6. D. Chauxian, R. A. Zatorski, H. Herman, and D. Oh, Oxide Powders for Plasma Spraying--The Relationship Between Powder Characteristics and Coating Properties, *Thin Solid Films*, Vol 118, 1984, p 467-475.
7. E. Lugscheider and I. Rass, Underwater Plasma Spraying of Stabilized Zirconia for Thermal Barrier Coatings, *J. Thermal Spray Tech.*, Vol 1, No. 1, 1992, p 49-56.

8. M. Yasuda, F. Weinberg, and D. Tromans, Pitting Corrosion of Al and Al-Cu Single Crystals, *J. Electrochem. Soc.*, Vol 137, 1990, p 3708-3715.
9. F. W. Gayle, A. J. Shapiro, F. S. Biancaniello, and W. J. Boettinger, The Al-Cu-Fe Phase Diagram: 0 to 25 At. Pct Fe and 50 to 75 At. Pct Al-Equilibria Involving the Icosahedral Phase, *Met. Trans. A*, Vol 23A, 1992, p 2409-2417.
10. D. Gratias, Y. Calvayrac, J. Devaud-Rzepski, F. Faudot, M. Harmelin, A. Quivy, and P.A. Bancel, The Phase Diagram and Structures of the Ternary Al-Cu-Fe System in the Vicinity of the Icosahedral Region, *J. Non-Crystall. Solids*, Vol 153 & 154, 1993, p 482-488.
11. J. Shield, University of Utah, Department of Materials Science and Engineering, Salt Lake City, Utah, 84112, private communication.

CHAPTER 3:
PARTICLE SIZE EFFECTS ON CHEMISTRY AND
STRUCTURE OF Al-Cu-Fe QUASICRYSTALLINE COATINGS

A paper submitted to the *Journal of Thermal Spray Technology*

D. J. Sordélet, M. F. Besser and I. E. Anderson

Ames Laboratory, U. S. DOE, Iowa State University
Ames, IA 50011

Abstract

Gas atomized $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders of varying size fractions were plasma arc sprayed onto hot ($\sim 600^\circ\text{C}$) and cool ($\sim 25^\circ\text{C}$) substrates using Mach I and subsonic plasma gun configurations. The chemical composition and phase contents of coatings were determined. Furthermore, coatings were annealed in vacuum at 700°C for two hours to observe phase changes. It was found that finer particles (e.g., $<25\ \mu\text{m}$) tend to vaporize Al during spraying, which shifts the coating composition away from the quasicrystalline (ψ) single-phase region in the Al-Cu-Fe phase diagram. Coatings deposited on hot substrates were denser, richer in the ψ phase and harder than the corresponding coatings deposited onto cool substrates.

[Key Words: Quasicrystal, Al-Cu-Fe coatings, particle size effects, coating chemistry, coating microstructure]

1. Introduction

Quasicrystals have previously forbidden rotational symmetries (e.g., five-fold) and lack periodic translational order (1). Since the unexpected discovery of quasicrystalline structure in 1984 (2), research studies have mostly focused on understanding atomic structure (3) and phase equilibrium (4,5). More recently, scientists have begun to recognize the potential usefulness of quasicrystals in engineering applications (6,7). For example, the hardness and stiffness characteristics of quasicrystals formed from the Al-Cu-Fe system suggests that the materials should exhibit low-friction, wear resistant behavior (8). Indeed, a number of studies have supported this hypothesis (9,10). Other research has shown that some Al-based quasicrystals are resistant to excessive oxidation (11-13).

To date, hundreds of metal alloys have been identified to display a quasicrystalline phase (14). Many quasicrystalline systems require rapid solidification methods, such as melt spinning, in order to form. Tsai, et al. found that the Al-Cu-Fe system forms a quasicrystalline phase which is stable at temperatures very close to its melting point (15). This discovery has precipitated numerous efforts to characterize the mechanical properties of Al-Cu-Fe quasicrystals (16,17). A portion of the research within our own laboratory is aimed at evaluating plasma arc sprayed (PAS) quasicrystal coatings for automotive and agricultural applications. In addition, the attractive economical and environmental features of Al-Cu-Fe alloys have motivated studies to evaluate quasicrystal coatings as replacements for electro-deposited chromium coatings.

One feature of the Al-Cu-Fe system, which has hindered the synthesis of macroscopic, single-phase, single-grain quasicrystals, is its complex solidification behavior. This alloy system was characterized well over fifty years ago (18,19). It is interesting to note that this early work identified a complex phase centered approximately around $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$. The authors were unable to define this phase, which they termed as ψ , using X-ray diffraction. It is now known that the ψ phase has a quasicrystalline structure. More recent surveys of the

Al-Cu-Fe system have been performed to better understand the phase relationships between the ψ phase and its neighboring crystalline phases (5). Note that a composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ was used throughout the current study. This composition falls within the single-phase ψ region of the Al-Cu-Fe phase diagram. The ψ phase has equilibrium relationships with a cubic (β) phase and a monoclinic (λ) phase. Typical compositions of the β and λ phases that formed during processing (e.g., chill casting) are $\text{Al}_{55}\text{Cu}_{40}\text{Fe}_5$ and $\text{Al}_{72}\text{Cu}_5\text{Fe}_{23}$, respectively. These phases have been described in more detail elsewhere (20).

Starting powders are well-known to strongly affect the microstructure and properties of PAS coatings (21). Consideration of starting powders is especially critical when forming Al-Cu-Fe quasicrystal PAS coatings due to the complex solidification path of the alloy. Recent studies by the authors demonstrated that gas atomized $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders produced coatings which were much more homogeneous in chemical composition and phase structure than coatings prepared from powders obtained by crushing a cast ingot (20). These differences were clearly the result of the contrasting solidification rates between the gas atomization and ingot casting processes; the former process yields much more homogeneous powders.

While it is important to have homogeneous starting powders if a uniform coating microstructure is desired, it is equally necessary to have coating parameters which do not alter the composition of the powder. For example, metal carbides can easily decompose and oxidize during PAS and form undesirable phases (22,23). Similar difficulties can be encountered with alloy powders if selective vaporization of a particular element occurs. Material loss due to vaporization has been reported to occur during air plasma spraying of ceramic superconductors (24). It is quite likely that the problem of material loss is more wide-spread throughout the PAS industry than is currently realized due to the lack of appropriate analytical capabilities in many coating facilities.

In the development of Al-Cu-Fe PAS coatings, it is generally desired to maximize the fraction of the quasicrystal (ψ) phase. Furthermore, coatings intended for tribological

applications typically require minimal porosity. Initial studies in our laboratory revealed that when using gas atomized $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder, finer starting powders produced higher densities, while coarser particles produced more of the ψ phase. These general observations were made while keeping all other processing parameters constant. The objective of the current study is to understand the role of starting powder particle size on PAS coating chemistry, phase equilibrium and grain structure.

2. Experimental Procedure

2.1 Starting Powders

Starting powders with a nominal composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ were prepared by gas atomization using argon. Powders were screened or air classified into different particle size distributions for subsequent PAS. The specific size fractions prepared are shown below.

- -25 μm
- +25, -45 μm
- +53, -63 μm
- +45, -75 μm
- +75, -106 μm

The as-atomized powder is primarily a two-phase mixture of the ψ and β phases. Therefore, portions of the five different powder sizes were annealed under vacuum at 700°C for 14 hours to form nearly single-phase ψ structures.

2.2 Plasma Arc Spraying

The as-atomized and vacuum annealed starting powders were processed by PAS using subsonic and Mach I plasma gun configurations. The gun components and operating parameters are listed in Table 1. The conditions shown in Table 1 were not selected to obtain a specific set of plasma temperatures or particle velocities. Rather, they were chosen in an

Table 1. Plasma gun configurations and spraying parameters

Parameter	Mode	
	Mach I	Subsonic
Plasma gun	SG-100*	SG-100*
Anode (part number)	358	730
Cathode (part number)	112	120
Gas injector (part number)	113	112
Amps	800	700
Volts (@gun)	43.1	25.7
Arc gas (slpm)	37.8 (Ar)	37.8 (Ar)
Aux gas (slpm)	20.0 (He)	0
Carrier gas (slpm)	5.6 (Ar)	5.6 (Ar)
Powder feed rate (g/min)	20.0	20.0
Stand off (cm)	7.5	7.5

*Miller Thermal, Inc.

attempt to establish a reasonable variation in power input and gas velocity so that differences in particle heating and in-flight reactivity could be observed.

The effect of substrate temperature was also studied during PAS of the different powder sizes. Copper substrates were heated in a furnace until they reached approximately 650°C. The substrates were removed and spraying was initiated within a few seconds. Mild steel substrates were fixtured next to the Cu tiles during spraying. The steel substrates were air cooled from behind during coating. Also a thin (~0.1 cm) strip of mild steel, which was

likewise air cooled from behind, was coated along with the Cu and steel substrates. The material deposited onto the thin strip of steel was removed for subsequent characterization.

The approximate temperatures of the Cu and steel substrate surfaces were continuously monitored by placing a Type-K thermocouple into a hole drilled into the back of substrates. The tip of the thermocouple was 0.1 cm away from the surface being coated. Figure 1 shows a typical temperature profile of hot Cu and cool steel substrates during coating. Very similar temperature behavior was seen during all coating experiments.

A small piece of each coated steel substrate was heated in vacuum at 700°C for two hours to study the microstructural evolution of the as-sprayed material.

Coating samples discussed throughout the text will be labeled as given in Table 2 according to starting powder size (1, 2, 3, 4 or 5), PAS gun configuration (M or S) and substrate temperature (H or C). The powder size labels 1, 2, 3, 4 and 5 correspond, respectively, to the -25 μm ; +25, -45 μm ; +53, -63 μm ; +45, -75 μm and +75, -106 μm size fractions. The coatings prepared with starting powders that were vacuum annealed will be identified with an asterisk (*) following the powder size label. The PAS gun configuration labels M and S refer to Mach I and subsonic, respectively. The coatings deposited onto hot Cu substrates will be labeled H, while those deposited onto cool steel substrates will be labeled C. For example, the coating sprayed with -25 μm powder onto a hot Cu substrate using the Mach I gun assembly will be described as 1MH. Table 2 provides a complete description of the coatings prepared in this study and their corresponding sample codes.

2.3 Characterization

The techniques described below were used to characterize starting powders and PAS coatings. As-sprayed, i.e., bulk, coatings and powdered coatings (after removal from their substrate) were studied.

Figure 1. Typical temperature profile of (a) Cu substrate; and (b) steel substrate during plasma arc spraying.

Table 2. Coating sample descriptions

Coating Label	Starting Powder Size (μm)	Powder Condition	Gun Configuration	Substrate Condition
1MH	-25	As-atomized	Mach I	Hot
2MH	+25, -45	"	"	"
3MH	+53, -63	"	"	"
4MH	+45, -75	"	"	"
5MH	+75, -106	"	"	"
1MC	-25	"	"	Cool
2MC	+25, -45	"	"	"
3MC	+53, -63	"	"	"
4MC	+45, -75	"	"	"
5MC	+75, -106	"	"	"
1SH	-25	"	Subsonic	Hot
2SH	+25, -45	"	"	"
3SH	+53, -63	"	"	"
4SH	+45, -75	"	"	"
5SH	+75, -106	"	"	"
1SC	-25	"	"	Cool
2SC	+25, -45	"	"	"
3SC	+53, -63	"	"	"
4SC	+45, -75	"	"	"
5SC	+75, -106	"	"	"
1*MH	-25	Annealed	Mach I	Hot
4*MH	+45, -75	"	"	"
5*MH	+75, -106	"	"	"
1*MC	-25	"	"	Cool
4*MC	+45, -75	"	"	"
5*MC	+75, -106	"	"	"
1*SH	-25	"	Subsonic	Hot
4*SH	+45, -75	"	"	"
5*SH	+75, -106	"	"	"
1*SC	-25	"	"	Cool
4*SC	+45, -75	"	"	"
5*SC	+75, -106	"	"	"

Inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine Al, Cu and Fe contents of starting powders and powdered coatings. Oxygen contents of the powders and coatings were measured using the inert gas fusion (IGF) technique on a Leco 12 system. Note that the coating samples for the above chemical analyses were obtained by removing them from the thin steel strips described earlier.

X-ray diffraction (XRD) was used to determine the structures of starting powders, as-sprayed coatings and powdered coatings. Powdered coating samples were obtained from material deposited onto hot Cu substrates and thin steel strips. X-ray diffraction was performed with a Phillips 1810 diffractometer using $\text{CuK}\alpha$ radiation. Due to the large number of coating samples generated in the current study, most scans were performed between 42° and 46° two-theta. The primary peaks from the ψ and β phases fall within this range when using a $\text{CuK}\alpha$ source.

It is difficult to quantify the amounts of the ψ , β and λ phases using XRD data. Conventional quantitative methods using structure factors are not straightforward due to the unknown atomic positions of the quasicrystalline ψ phase. An effort to obtain some quantitative information was made by blending known amounts of single-phase ψ and β phase powders together. These powders were obtained from vacuum annealed cast ingots with compositions determined from previous research (20). The XRD patterns obtained from the blended mixtures were analyzed by comparing specific peak intensities.

Differential thermal analysis (DTA) was performed to compare the thermal events during heating of starting powders and powdered coatings. The DTA results were obtained with a Perkin Elmer System 7 unit. Scans were performed in flowing argon at a heating rate of $10^\circ\text{C}/\text{min}$. Approximately 50 mg of powder coating was analyzed in each run.

Coatings deposited onto hot Cu and cool steel substrates were prepared for metallographic examination. Epoxy mounts were prepared by vacuum impregnation of the coating. Grinding and polishing was performed on an automatic system using an initial 180-

grit SiC paper followed by 9 and 3 μm lapping. A final polish with 0.05 μm Al_2O_3 was used to remove final scratches. Polished cross sections were observed using scanning electron microscopy (SEM) on a JOEL 6100 instrument.

Indentation hardness measurements were taken from polished coatings. Samples of several coatings deposited onto hot Cu and cool steel substrates were tested with a Vickers indenter using a 30 g load. Hardness values reported represent an average of five measurements.

3. Results

3.1 Composition and structure of starting powders

The chemical compositions of the five starting powder size fractions determined by ICP-AES are displayed in Table 3. All powders are similar in Al, Cu and Fe contents and are close to the targeted starting composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$. The bulk oxygen content clearly decreased with increasing average particle. This strongly suggests that oxygen is present as a surface layer rather than a uniform bulk constituent.

Table 3. Chemical compositions of gas atomized starting powders

Powder size (μm)	Al (w/o) $\ddagger$	Cu (w/o) $\ddagger$	Fe (w/o) $\ddagger$	O (w/o)	% ψ^* (w/o)
-25	42.4	39.7	16.4	0.205	69
+25, -45	42.3	39.7	16.9	0.112	63
+53, -63	42.1	39.8	16.9	0.083	60
+45, -75	42.0	39.9	16.7	0.080	60
+75, -106	42.0	40.5	16.4	0.065	55

* w/o of ψ phase based on calibration curve in Figure 5.

$\ddagger$ Note: Composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ in w/o is approximately 42.3w/o Al, 40.0w/o Cu and 17.7w/o Fe.

The structures of the as-atomized powders are shown in Figure 2. Also shown are XRD patterns obtained from the starting powders after vacuum annealing at 700°C for 12 hours. The as-atomized powders contain the quasicrystalline (ψ) and cubic (β) phases. As mentioned earlier, the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ composition also has equilibrium relationships with a monoclinic (λ) phase. However, its presence in the powder samples is difficult to determine by XRD because of the large number of scattering planes present in the low-symmetry monoclinic structure. The vacuum annealing produced a mostly single-phase ψ structure in all powder sizes; however, some of the cubic β phase remained.

The consistency of phases between powder sizes can further be seen by comparing DTA patterns. Figure 3 shows the melting behavior of the -25 μm and +45, 74 μm size fractions. The endothermic peak just below 900°C represents the decomposition of ψ into liquid and $\beta + \lambda$. The higher temperature peaks correspond to final melting. The coarser powder (Fig. 3b) does show an additional endothermic reaction between 600 and 700°C. This is likely melting of an Al_2Cu -type phase, which is often seen with $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ composition. under slower solidification conditions (e.g., ingot casting) (25).

Powder morphology and internal structure of the different powder size fractions are presented in Figure 4. The -25 μm powder has a large population of particles which are below 10 μm . It is not clear whether or not these are satellites which broke loose during size classification. The +53, -63 μm size fraction (Fig. 4c) actually appears to be a bimodal distribution; the smaller particles again may have originated from satellites. The polished cross sections illustrate the mixed-phase structure of the atomized particle. The coarser particles tend to show a slightly dendritic structure, while the cellular growth is more dominant in smaller particles.

Figure 2. XRD patterns of as-atomized and annealed starting powders. Powder size fractions are as follows: (a) -25 μm ; (b) -25 μm annealed; (c) +25, -45 μm ; (d) +45, -75 μm ; (e) +45, -75 μm ; (f) +53, -63 μm annealed; (g) +75, -106 μm ; and (h) +75, -106 μm annealed.

Figure 3. DTA thermograms obtained while heating (a) -25 μm ; and (b) +75, -106 μm as-atomized starting powders.

Figure 4. SEM micrographs of as-atomized starting particles. Images shown are powder morphology and polished cross sections of the following particle size fractions: (a) $-25\ \mu\text{m}$, (b) $+25, -45\ \mu\text{m}$, (c) $+53, -63\ \mu\text{m}$, (d) $+45, -75\ \mu\text{m}$ and (e) $+75, -106\ \mu\text{m}$

(a)

(b)

(c)

(d)

(e)

3.2 Composition and structure of PAS coatings

The chemical analysis results from coatings removed from hot Cu substrates and thin steel strips are listed in Table 4. The $-25\text{ }\mu\text{m}$ starting powder lost considerable Al during spraying (coatings 1MH, 1MC, 1SH, 1SC, 1*MH, 1*MC, 1*SH and 1*SC). The $+25, -45\text{ }\mu\text{m}$ size fraction powder exhibited similar mass loss during spraying, but to a lesser extent. Also, comparison of compositions (e.g., lower Al contents) of coatings sprayed with Mach I and subsonic gun arrangements suggests that the latter configuration and corresponding operating parameters (Table 1) produced a more aggressive environment. This observation is more easily seen with smaller powder size fraction coatings (e.g., 1SC, 2SC, 3SC vs. 1MC, 2MC and 3MC, respectively).

Oxygen contents of as-sprayed coatings (Table 4) also varied as a function of the starting powder particle size. Higher O values were measured from the finer powder fractions. In addition, coatings sprayed with the subsonic gun configuration picked up more O than the coatings sprayed with the Mach I configuration; similar behavior between the two spraying conditions was also observed with the annealed starting powder. During spraying, the annealed starting powders gained slightly more O than the as-atomized powders. For a given powder particle size and gun configuration, coatings deposited onto the hot Cu substrates gained more O than the comparable coatings deposited onto the cool steel substrates.

Figure 5 displays the peak height ratios from ψ and β phases as a function of ψ content. The data presented in Figure 5 were obtained by comparing the (100000) and (110) peak intensities from the ψ and β phases, respectively. The six independent Miller indices used to identify the icosahedral phase are discussed in Reference 15. Very similar results were obtained by comparing the (110000) and (101000) ψ peaks to the (110) and (211) β peaks, respectively. The two-theta locations of these specific peaks are identified in Figure 2a. These

Table 4. Chemical composition and ψ phase content of PAS coatings

Coating Label	Al (w/o)‡	Cu (w/o)‡	Fe (w/o)‡	O (w/o)	% ψ * (w/o)
1MH	35.9	40.9	17.1	2.21	24
2MH	39.0	41.3	16.2	1.15	71
3MH	40.9	39.9	16.3	0.738	70
4MH	41.6	40.2	16.0	0.552	69
5MH	41.7	40.5	16.3	0.456	69
1MC	36.1	42.0	18.6	1.74	10
2MC	40.0	40.7	16.9	0.557	15
3MC	40.7	39.9	16.9	0.294	37
4MC	41.5	39.9	16.9	0.154	43
5MC	40.9	39.7	16.9	0.145	50
1SH	31.3	44.1	19.2	2.43	7
2SH	37.3	41.7	17.4	1.49	20
3SH	38.6	39.8	16.1	0.912	54
4SH	41.3	40.2	16.2	0.594	77
5SH	41.7	39.8	16.2	0.447	79
1SC	29.6	42.8	21.0	2.04	2
2SC	35.3	42.3	18.7	0.971	4
3SC	39.6	40.4	17.1	0.604	28
4SC	40.7	40.1	16.8	0.267	59
5SC	41.0	40.0	16.6	0.231	61
1*MH	31.7	44.4	17.9	-	12
4*MH	41.3	40.4	16.4	0.529	-
5*MH	40.9	40.5	16.3	0.657	71
1*MC	33.3	42.3	19.0	2.08	3
4*MC	40.6	39.7	16.3	0.242	43
5*MC	40.5	39.4	16.3	0.242	42
1*SH	28.0	45.0	20.2	-	4
4*SH	39.4	41.1	16.6	0.764	-
5*SH	39.2	41.9	16.1	0.998	70
1*SC	30.3	42.9	20.5	2.24	2
4*SC	40.0	40.0	16.7	0.332	52
5*SC	40.1	39.7	16.4	0.303	48

* w/o of ψ phase from powdered coatings are based on calibration curve in Figure 5.

‡ Note: Composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ in w/o is approximately 42.3w/o Al, 40.0w/o Cu and 17.3w/o Fe.

Figure 5. Weight percent of ψ phase in a binary mixture of ψ and β powders as determined by peak intensity ratios of (100000) and (110) planes for ψ and β phases, respectively.

results provide a semi-quantitative determination of phase contents in as-sprayed coatings discussed later. The curve in Figure 5 was also used to estimate relative phase fractions in the as-atomized starting powders (Table 3).

Figures 6 and 7 display XRD patterns obtained from coatings deposited onto hot Cu and cool steel substrates using Mach I and subsonic plasma gun configurations, respectively. Each figure shows the differences in coating structure as a result of substrate temperature, i.e., hot Cu and cool steel substrates. Generally, a hot substrate appears to promote the formation

Figure 6. XRD patterns of PAS coatings deposited onto hot Cu and cool steel substrates using a Mach I gun configuration and the following starting powder particle sizes: (a) $-25\ \mu\text{m}$; (b) $+25, -45\ \mu\text{m}$; (c) $+53, -63\ \mu\text{m}$; (d) $+45, -75\ \mu\text{m}$; and (e) $+75, -106\ \mu\text{m}$. Refer to coating labels to distinguish different substrates.

Figure 7. XRD patterns of PAS coatings deposited onto hot Cu and cool steel substrates using a subsonic gun configuration and the following starting powder particle sizes: (a) $-25\ \mu\text{m}$; (b) $+25, -45\ \mu\text{m}$; (c) $+53, -63\ \mu\text{m}$; (d) $+45, -75\ \mu\text{m}$; and (e) $+75, -106\ \mu\text{m}$. Refer to coating labels to distinguish different substrates.

of the ψ phase. Comparison of Figures 6 and 7 shows that the coatings which were sprayed using the Mach I gun configuration and smaller starting particle sizes (e.g., powder sizes 1, 2 and 3) developed more of the ψ phase. The phase contents of the coatings formed with annealed starting powders (Figs. 8 and 9) are similar to the coatings prepared with the as-atomized powders.

Coatings deposited onto hot Cu substrates are not structurally uniform throughout their thickness. Figures 10 and 11 illustrate the variations in ψ and β contents of as-sprayed coating surfaces and powdered coatings. Note that these figures show XRD data obtained from coatings deposited onto hot Cu substrates. Analysis of a powdered coating by XRD represents an average phase assemblage throughout the thickness of the coating. In contrast, XRD of an as-sprayed coating surface examines only a few microns of deposited coating. In this study, coating thickness ranged from around 300 μm to near 700 μm ; coarser powder particle sizes produced thicker coatings. The differences between the XRD patterns obtained from as-sprayed surfaces and powdered coatings illustrate the variation of phases throughout the bulk of the coatings. Identical analyses of as-sprayed coating surfaces and powdered coatings were performed on coatings deposited onto cool steel substrates. Although not shown here, there was no discernible difference between the XRD patterns obtained from as-sprayed surfaces and powdered coatings deposited onto the cool steel substrates. Coatings formed with annealed starting powders followed the same trend as the coatings formed with as-atomized powders deposited onto the hot Cu and cool steel substrates.

Sections of cool steel substrates coated with the different powder size fractions were vacuum annealed at 700°C for two hours. The XRD patterns obtained from as-sprayed surfaces of annealed coatings prepared with as-atomized and annealed starting powders are given in Figure 12 and 13, respectively. Note that the coatings were not removed from their substrates prior to annealing. The XRD patterns in Figures 12 and 13 reveal that coatings formed with coarser starting powder particle sizes (e.g., >53 μm) and the Mach I gun

Figure 8. XRD patterns of PAS coatings deposited onto hot Cu and cool steel substrates using a Mach I gun configuration and the following annealed starting powder particle sizes: (a) $-25\ \mu\text{m}$; (b) $+45, -75\ \mu\text{m}$; and (c) $+75, -106\ \mu\text{m}$. Refer to coating labels to distinguish different substrates.

Figure 9. XRD patterns of PAS coatings deposited onto hot Cu and cool steel substrates using a subsonic gun configuration and the following annealed starting powder particle sizes: (a) -25 μm ; (b) +45, -75 μm ; and (c) +75, -106 μm . Refer to coating labels to distinguish different substrates.

Figure 10. XRD patterns of as-sprayed and powdered PAS coatings deposited onto hot Cu substrates using a Mach I gun configuration and the following starting powder particle sizes: (a) $-25\ \mu\text{m}$; (b) $+25, -45\ \mu\text{m}$; (c) $+53, -63\ \mu\text{m}$; (d) $+45, -75\ \mu\text{m}$; and (e) $+75, -106\ \mu\text{m}$. Refer to figure legend to distinguish between as-sprayed and powdered samples.

Figure 11. XRD patterns of as-sprayed and powdered PAS coatings deposited onto hot Cu substrates using a subsonic gun configuration and the following starting powder particle sizes: (a) $-25\ \mu\text{m}$; (b) $+25, -45\ \mu\text{m}$; (c) $+53, -63\ \mu\text{m}$; (d) $+45, -75\ \mu\text{m}$; and (e) $+75, -106\ \mu\text{m}$. Refer to figure legend to distinguish between as-sprayed and powdered samples.

Figure 12. XRD patterns of vacuum annealed (700°C) PAS coatings deposited onto cool steel substrates using the following starting powder particle sizes: (a) -25 μm ; (b) +25, -45 μm ; (c) +53, -63 μm ; (d) +45, -75 μm ; and (e) +75, -106 μm . Refer to figure legend to distinguish between different gun configurations.

Figure 13. XRD patterns of vacuum annealed (700°C) PAS coatings deposited onto cool steel substrates using the following annealed starting powder particle sizes: (a) -25 μm ; (b) +45, -75 μm ; and (c) +75, -106 μm . Refer to figure legend to distinguish between different gun configurations.

configuration develop a nearly single-phase ψ structure during vacuum annealing. Coatings deposited using the subsonic gun configuration, with the exception of coating 5SC, generally do not form a single-phase ψ structure, i.e., the cubic β phase is still present.

While the different starting powder size fractions exhibited comparable melting behavior (Fig. 3), the PAS coatings formed with different powder particle sizes showed contrasting behavior. Figure 14 shows DTA traces obtained from coatings 1SC and 4SC. The finer powder coating, 1SC, does not show a thermal event associated with the ψ phase, i.e., an endothermic peak just below 900°C. The coarser powder coating, 4SC, on the other hand, shows similar melting behavior to the +45, -75 μm starting powder. Very similar DTA results were obtained with coatings sprayed with the Mach I gun configuration as well as with annealed starting powders. In general, coatings which lost more Al during spraying produced DTA traces similar to Figure 14a.

Variations in coating grain structures paralleled the chemical and structural differences discussed above. Coatings deposited onto the hot Cu substrates are denser and show less intergranular cracking than their counterparts sprayed onto cool steel substrates. Figure 15 displays polished cross sections of coatings sprayed with the Mach I plasma gun configuration onto hot and cool substrates. The dense layer at the coating substrate interface on the hot Cu substrates is an oxide layer which formed while preheating the Cu substrate. Coating density also varies with starting powder size. Regardless of the substrate temperature, coatings prepared with coarser particles are more porous. Coatings deposited with the subsonic plasma gun configuration exhibit very similar microstructures to the coatings shown in Figure 15. Annealing the starting powder did not produce any noticeable differences in the grain structure of the PAS coatings.

Indentation hardness measurements from selected coating samples are displayed in Table 5; average values are shown $\pm$ one standard deviation. Coating hardness appears to increase with higher coating density and higher ψ phase content; however, higher hardness

Figure 14. DTA thermograms obtained while heating PAS coatings deposited onto cool steel substrates using a subsonic gun configuration and the following starting powder particle sizes: (a) -25 μm ; and (b) +45, -75 μm .

Figure 15. SEM micrographs of PAS coatings formed with a Mach I gun configuration on hot Cu substrates (left hand column) and cool steel substrates (right hand column) using the following starting powder particle sizes: (a) and (b) $-25\text{ }\mu\text{m}$; (c) and (d) $+25, -45\text{ }\mu\text{m}$; (e) and (f) $+53, -63\text{ }\mu\text{m}$; (g) and (h) $+45, -75\text{ }\mu\text{m}$; and (i) and (j) $+75, -106\text{ }\mu\text{m}$.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

(j)

values on coatings formed with $-25\text{ }\mu\text{m}$ powders may also be due to the presence of oxides within the coating microstructure.

4. Discussion

4.1 Coating chemistry

It is evident from Table 3 that the compositions of the atomized powders do not vary as a function of particle size. Oxygen levels of the atomized powders are higher in the finer, larger surface area powders. As discussed earlier, this strongly suggests that oxygen contamination is present as a surface film rather than as a bulk constituent. Also, results from the XRD (Fig. 2) and DTA (Fig. 3) analyses show the fairly uniform phase structure of the different powder particle size fractions. The coarser starting powder particles have slightly more of the β phase, as shown in Figure 2e and Table 3. Considering the uniformity of the starting powders, the chemistry changes measured in the as-sprayed coatings (Table 4) clearly occurred during spraying.

All the coatings appear to have lost some Al during spraying; however, coatings formed with finer powders show a substantial loss of Al. This is consistent with both plasma gun configurations and with the as-atomized and annealed starting powders. The coatings which lost the most Al also gained the most oxygen. The annealed starting powders tended to slightly gain more oxygen and lose more Al during spraying than the as-atomized starting powders. Assuming that similar size powders are all molten during spraying, the contrasting starting phase structures of the chemically-similar as-atomized and annealed starting powders should not affect the phase structure of the coatings. The chemical variations seen in the coatings formed with as-atomized and annealed powders are therefore likely due to initial reactions between the particles and the plasma. For example, if the thermal conductivities of the ψ and β phases are different, then the thermal behavior of multi-phase as-atomized and single-phase annealed powders could be different during spraying. The similar compositions of as-sprayed

coatings deposited onto hot Cu and cool steel substrates show that substrate temperature does not influence final coating chemistry. Therefore, the variation between starting powder and coating composition (e.g., loss of Al) must be occurring prior to deposition onto the substrate.

While it is likely that the oxygen incorporated into the coating during spraying is in the form of Al_2O_3 (11), the level of oxygen measured by IGF does not account for the total loss of Al. Also, the dissolution technique used to prepare samples for ICP-AES analysis did not leave any residual solid (e.g., Al_2O_3); therefore, Al present as an oxide should be part of the reported values in Table 4. Given this consideration, it appears that Al is lost by vaporization during spraying. If sufficient thermal energy is present to volatilize a portion of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders, Al is the most susceptible to vaporization. The vapor pressure of pure Al at temperatures between 1000 and 2000°C is much higher than the vapor pressure of Cu or Fe (26).

The reasons for the increased loss of Al in the coatings sprayed with the subsonic plasma gun configuration are not clear. The power consumed by subsonic spraying was around 18 kW, while Mach I spraying consumed around 27 kW. However, plasma gas composition and velocity need to be considered as well to predict plasma-powder interactions. Qualitatively, the subsonic parameters provide either more thermal energy to the powders, which increases Al vaporization, or less kinetic energy, which extends the time for vaporization before solidification.

Selective elemental loss during PAS of alloy powders is not uncommon. Perhaps the most well-known case is the decarburization of WC powders during air plasma spraying (22,23). Similar reactions leading to mass loss have been observed in spraying other refractory metal carbides (27). Since the reaction products in these examples include volatile species, the material loss is straightforward to understand. Selective vaporization of elements which exist as condensed phases under normal conditions has been observed as well. For example, air plasma spraying of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor powders resulted in the loss of

Cu (24). Furthermore, recent results have shown that fine $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders (e.g., +5, -25 μm) also lost Al during low pressure plasma spraying within an argon atmosphere at 200 torr (28). On the other hand, studies of PAS of Al-based intermetallics (e.g., Ni_3Al - NiAl in a low pressure system) did not show any detectable loss of Al (29).

The difference in the tendency for selective elemental loss during PAS of Al-Cu-Fe quasicrystal and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders compared to that for Ni_3Al - NiAl powders is likely due to the former systems' lower melting temperatures and lower thermal conductivities. Typical thermal conductivities (in $\text{W/cm}\cdot\text{K}$) reported in the literature for $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and NiAl are 4 (31), 10 (32) and 75 (33), respectively. Two-phase, i.e., liquid and solid, heat conduction in a spherical particle can be seen from the following energy balance equations:

$$\rho_s C_s \frac{\partial T_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 k_s \frac{\partial T_s}{\partial r} \right) \quad 0 \leq r < r_f(t) \quad (1)$$

$$\rho_\ell C_\ell \frac{\partial T_\ell}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 k_\ell \frac{\partial T_\ell}{\partial r} \right) \quad r_f(t) \leq r \leq r_p \quad (2)$$

In equations (1) and (2), ρ is particle density, C is specific heat, T is temperature, k is thermal conductivity, r_p is particle radius and $r_f(t)$ is the radius of the dynamic solid-liquid boundary. Subscripts s and ℓ refer to solid and liquid states, respectively. The energy balance helps to illustrate how a lower thermal conductivity would require additional time for a particle to become fully molten. This may lead to increased surface liquid temperatures, which would further enhance vaporization. Alloy powders with elemental constituents that have contrasting vapor pressures will therefore be particularly susceptible to selective elemental loss.

Modeling studies have been performed to simulate the melting of various size spherical Fe particles within an RF-plasma at atmospheric pressure (30). They predict that smaller particles will more quickly reach a molten state where the additional heat flux available to the

particle is used to supply the heat of vaporization. The model estimates that for an assumed set of plasma conditions, a 20 μm diameter Fe particle would vaporize in 3 ms, while a 60 μm diameter Fe particle would require around 60 ms to vaporize. This shows the extreme sensitivity of particle size to heat conduction and potential vaporization. These observations are in agreement with the results of the current study and imply that small, lower thermal conductivity powders are more sensitive to mass loss through vaporization.

4.2 Coating structure

The shifts in powder chemistry discussed above have a direct impact on the phase structure of the deposited coatings. The substantial loss of Al while spraying the -25 μm powder produced coatings which were all nearly single-phase β as determined by XRD (Figs. 6, 7, 8 and 9). Coatings prepared with +25, -45 μm powder using the subsonic arrangement also consist mostly of the β phase (Fig. 7b). Coatings prepared with larger starting powder particle sizes lost less Al and formed coatings which contain ψ and β phases (Figures 6-9). The volume of the ψ phase increases with increasing starting powder particle size (Table 4).

The phases formed during coating are not only affected by compositional changes, as discussed above, but also by substrate thermal effects. Coatings sprayed onto hot Cu substrates developed more of the ψ phase than their counterparts deposited onto cool steel substrates (Table 4 and Figs. 6-9). The increased formation of the ψ phase on the hot Cu substrates is likely due to annealing of the solidified coating during coating. Since the ψ phase is stable at slightly above the estimated substrate surface temperatures (5), some phase homogenization during annealing may have occurred concurrently with spraying. The driving force would come from the heat provided by the Cu substrate together with the heat of impacting molten droplets. This latter contribution would be more pronounced with the hot Cu substrates than with the cool steel substrates because the higher temperature reduces the thermal gradient between the impacting droplets and the Cu substrate or, as coating progresses, the

freshly deposited coating surface. This could also provide additional time for annealing to occur in the presence of liquid, which would enhance diffusion and phase homogenization.

The temperature of the coating surface appears to decrease with each sequential coating layer deposited onto the hot Cu substrates. This can be seen by comparing the XRD patterns obtained from as-sprayed surfaces and from powdered coatings. The as-sprayed coating surfaces represent a coating deposited onto a relatively cooler surface since X-ray penetration is only on the order of 5-10 μm . The powdered coating represents an integrated series of coating surface temperatures, which would have a higher average substrate temperature than the final as-sprayed surface. Figures 10 and 11 show the higher ψ phase content of the powdered coating samples. The decreasing surface temperature of the coating during spraying effectively reduces the amount of annealing which can occur. The Mach I and subsonic coatings sprayed with the annealed starting powders onto hot Cu substrates exhibited the same behavior as the coatings shown in Figure 10 and 11. The XRD patterns obtained from as-sprayed surfaces and powdered samples of coating deposited on cool steel substrates, however, did not show any differences in ψ or β phase contents. Since the steel substrates were cooled during spraying, no annealing would be expected to occur and the as-sprayed surface will be more similar to the bulk of the coating.

The roles of chemistry and solidification behavior on coating structure can be further understood by evaluating the XRD data obtained from coatings deposited onto cool steel substrates which were subsequently vacuum annealed. For example, vacuum annealing of the 1MC and 1SC coatings did not change their structure (Fig. 12a). The 2SC coating did not change its structure during annealing, but the 2MC coating showed an increase in ψ phase (Fig. 12b). This latter change is more evident if the 2MC curve in Figure 12b is compared to the XRD trace from the as-sprayed 2MC coating shown in Figure 6b. Further increases in starting powder particle size resulted in coatings which formed higher ψ content coatings during vacuum annealing (Fig. 12c-e). The Mach I coatings sprayed with coarser particles (3MC,

4MC and 5MC) all developed a nearly single-phase ψ structure during annealing. The corresponding subsonic coatings followed the same trend but the 3SC and 4SC coatings still had some β phase present. The Mach I coatings formed with annealed starting powders behaved similarly, as shown in Figure 13. Coarser annealed powders sprayed with subsonic conditions (4*SC and 5*SC), however, still showed some residual β phase after annealing (Fig. 13b and c).

The above XRD results correlate very well with ICP-AES chemical analyses (Table 4). Powders which lose the most Al during spraying exhibit higher concentrations of the β phase in both as-sprayed and vacuum annealed conditions. The coatings which were measured to contain no more than 40 w/o Al follow this behavior. However, it is important to note that this value represents an average composition. Localized chemical inhomogeneities likely exist which control the observed change in phase distribution. Figure 14 shows further evidence of phase differences between coatings deposited with finer (4SC) particles. The 4SC coating clearly shows melting of the ψ phase below 900°C, followed by final melting of β and λ phases. The 1SC coating only shows one endothermic reaction around 1000°C, which likely corresponds to melting of the β phase. The final coating chemistry of the coatings which were low in Al could have shifted out of the ψ single phase region of the Al-Cu-Fe phase diagram. For example, the composition of the 2MC coating is approximately $\text{Al}_{61}\text{Cu}_{26}\text{Fe}_{12}$ (Table 4). According to a proposed isothermal section at 700°C (5), the composition of the 1SC coating has moved out of the single-phase ψ region into a ψ -rich portion of the two-phase region containing the β and ψ phases. Since $\text{Al}_{61}\text{Cu}_{26}\text{Fe}_{12}$ is a bulk value, there are likely localized compositional gradients throughout the coating which contribute to the XRD pattern obtained from coating 2MC shown in Figure 6b. Nevertheless, the chemistry and structure data clearly indicate that selective elemental loss during PAS will affect the resulting phase assemblage of the coating.

The results discussed above show that the phases developed in coatings sprayed with $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders depend upon both final chemistry and substrate thermal effects. Although most as-deposited coatings contain ψ and β phases, as long as they did not lose too much Al (e.g., $\sim 3\text{w/o}$) during spraying, the coatings may still be vacuum annealed to form a nearly single phase ψ structure. However, regardless of the substrate thermal history, if the coating loses enough Al during spraying, it will not form the quasicrystalline ψ phase during subsequent vacuum annealing. It is difficult to make absolute conclusions regarding phase equilibrium of the Al-Cu-Fe system with plasma sprayed coatings because of the unknown solidification path. Furthermore, surface oxidation could cause localized chemistry shifts if Al is further consumed to form an oxide. This effect has been seen during oxidation of Al-Cu-Fe powders and bulk coatings (13).

Starting powder particle size and substrate temperature affects the grain structure of the PAS coatings. Figure 15 displays SEM micrographs from polished cross sections of the Mach I coatings deposited onto hot and cool substrates. These coatings were sprayed with as-atomized powder. The subsonic coatings and the coatings formed with annealed starting powders were very similar to the coatings presented in Figure 15. The coatings sprayed onto hot Cu substrates are significantly less porous than those sprayed onto cool steel substrates. Particles contacting the hotter surface would be expected to exhibit increased deformation and liquid flow. In addition to variations in grain structure due to substrate temperature, Figure 15 also reveals the impact of starting powder particle size. The 1MH and 1MC coatings are denser than the coatings prepared with coarser powder particles. However, oxides are visible along the splat boundaries of the 1MH and 1MC coatings. The presence of oxides would be expected given the O gained during spraying of the finer powder particles (Table 4). Coarser starting powder particles lead to increased levels of porosity and intergranular cracking. The coatings sprayed with the coarser size fractions also contain unmelted particles. These are seen as areas with features similar to the solidified structure of the gas atomized powders (Fig. 4).

The variations in the as-sprayed coating microstructures produced different indentation hardness values. Data obtained from coatings prepared with a range of starting powder particle sizes are given in Table 5. The higher density and oxides present in the 1MH, 1MC, 1SH and 1SC coatings contribute to a higher hardness. Hardness values of coatings sprayed onto hot Cu substrates are higher than coatings formed on cool steel substrates. This is due to a combination of lower porosity and less of the ψ phase in these coatings. The β phase has been reported to be softer than the ψ phase within the Al-Cu-Fe system (8). Hardness measurements were not made with annealed powder coatings, but would be expected to show comparable results to those discussed above.

Table 5. Indentation Hardnesses of Plasma Air Sprayed Coatings

Coating Label	Indentation Hardness (Hv _{0.03})
1MH	1136 $\pm$ 337
1MC	704 $\pm$ 106
1SH	724 $\pm$ 186
1SC	675 $\pm$ 93
3MH	1039 $\pm$ 257
3MC	981 $\pm$ 134
3SH	909 $\pm$ 87
3SC	745 $\pm$ 94
5MH	859 $\pm$ 112
5MC	846 $\pm$ 178
5SH	890 $\pm$ 87
5SC	879 $\pm$ 157

5. Conclusions

Starting powder particle size is a universally important variable in thermal spraying processes. It is particularly critical in PAS of Al₆₃Cu₂₅Fe₁₂ powders. The low thermal conductivity of the quasicrystalline ψ phase provides greater opportunity to overheat and

partially vaporize powders during spraying. Finer particles (e.g., $\sim 25\ \mu\text{m}$) exhibited substantial vaporization of Al during PAS with Mach I and subsonic gun configurations. This material loss shifted the coating composition away from the single-phase ψ region of the Al-Cu-Fe phase diagram. Coatings which lost more than several atomic percent Al were mostly single-phase β , and did not change structure during vacuum annealing at 700°C . Coatings which lost less Al consisted of ψ and β phases in varying amounts depending on starting powder particle size and substrate temperature. These coatings could be annealed in vacuum at 700°C to form a nearly single-phase ψ structure.

The phases formed in the coatings were not only affected by chemistry shifts during spraying, but also by substrate temperatures. The heat provided by the hot Cu substrates appears to partially anneal the deposited coating during spraying. Coatings deposited onto hot substrates were denser, harder and richer in the ψ phase than coatings deposited onto cool substrates.

The results of this study show how critical it is to control powder particle size during PAS of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders. They also suggest that it is possible to further refine PAS parameters to produce denser coatings with higher ψ phase contents. Studies are in progress to further understand the role of other PAS conditions on $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ coating microstructure.

Acknowledgments

The authors would like to thank R. Hofer and C. Bradley for their expertise in performing the chemical analyses. M. Kramer is acknowledged for his discussions and creative suggestions. This study was performed at Ames Laboratory, Iowa State University, and was supported by the Director of Energy Research, Office of Basic Energy Sciences, United States Department of Energy under contract No. W-7405-ENG-82.

References

1. A. I. Goldman and M. Widom, Quasicrystal Structure and Properties, *Ann. Rev. Phys. Chem.*, Vol. 42, 1991, p.685-729.
2. D. Shechtman, I. Blech, D. Gratias and J. W. Cahn, Metallic Phase with Long-Range Orientational Order and No Translational Symmetry, *Phys. Rev. Lett.*, Vol. 53, No. 20, 1984, p.1951-1953.
3. C. Janot, J. M. Dubois and M. de Boissieu, Quasiperiodic Structures: another type of long-range order for condensed matter, *Amer. J. of Phys.*, Vol. 57, 1991, p.972-987.
4. D. Gratias, Y. Calvayrac, J. Devaud-Rzepski, F. Faudot, M. Harmelin, A. Quivy and P. Bancel, The Phase Diagram and Structures of the Ternary AlCuFe System in the Vicinity of the Icosahedral Region, *J. Non-Crystall. Solids*, Vol. 153 & 154, 1993, p.482-488.
5. F. W. Gayle, A. J. Shapiro, F. S. Biancaniello, and W. J. Boettinger, The Al-Cu-Fe Phase Diagram: 0 to 25 At. Pct Fe and 50 to 75 At. Pct Al-Equilibria Involving the Icosahedral Phase, *Met. Trans. A*, Vol. 23A, 1992, p.2409-2417.
6. J. M. Dubois, A. Proner, B. Bucaille, Ph. Cathonnet, C. Dong, V. Richard, A. Pianelli, Y. Massiani, S. Ait-Yazza and E. Belin-Ferre, Quasicrystalline Coatings with Reduced Adhesion for Cookware, *Ann. Chim. Fr.*, Vol. 19, 1994, p.3-25.
7. J. M. Dubois, S. S. Kang and J. Von Stebut, Quasicrystalline Low Friction Coatings, *J. Mater. Lett.*, Vol. 10, 1991, p.537-541.
8. U. Köster, W. Liu, H. Leibertz and M. Michel, Mechanical Properties of Quasicrystalline and Crystalline Phases in Al-Cu-Fe Alloys, *J. Non-Crystall. Solids*, Vol. 153 & 154, 1993, p.446-452.
9. J. M. Dubois, S. S. Kang and Y. Massiani, Application of Quasicrystalline Alloys to Surface Coatings of Soft Metals, *J. Non-Crystall. Solids*, Vol. 153 & 154, 1993, p.443-445.

10. E. Hornhogen and M. Schandl, Probing Mechanical Properties of Quasicrystalline Aluminum Alloys, *Z. Metallkd.*, Vol. 83, 1992, p.128-131.
11. S. L. Chang, W. B. Chin, C.-M. Zhang, C. J. Jenks and P. A. Thiel, Oxygen Absorption on a Single Grain, Quasicrystal Surface, *Surface Science*, in press 1995.
12. D. J. Sordélet, M. J. Kramer, I. E. Anderson and M. F. Besser, Microstructural Evolution, Oxidation and Wear of Al-Cu-Fe Quasicrystalline Coatings, *Int. J. of Modern Phys.*, in press 1995.
13. S. S. Kang and J. M. Dubois, Influence of the Annealing Atmosphere on the Formation of Al-Cu-Fe Quasicrystals, *J. Mater. Res.*, in press 1995.
14. K. F. Kelton, Quasicrystals: Structures and Stability, *Inter. Mater. Rev.*, Vol. 38, 1993, p.105-136.
15. A. P. Tsai, A. Inoue and T. Masumoto, A Stable Quasicrystal in Al-Cu-Fe, *Jpn. J. Appl. Phys.*, Vol. 26, 1987, p.L1505-1507.
16. S. S. Kang and J. M. Dubois, Compression Testing of Quasicrystalline Materials, *Philos. Mag. A*, Vol. 66, 1992, p.151-163.
17. J. Shield, M. J. Kramer and R. W. McCallum, Plastic Deformation in an Al-Cu-Fe Alloy, *J. Mater. Sci.*, Vol. 8, 1993, p.1199-1203.
18. A. J. Bradley and H. J. Goldschmidt, X-ray Study of Slowly Cooled Iron-Copper-Aluminum Alloys Part I.—Alloys Rich in Iron and Copper, *J. Inst. Met.*, Vol. 65, 1939, p.389-402.
19. A. J. Bradley and H. J. Goldschmidt, An X-ray Study of Slowly Cooled Iron-Copper-Aluminum Alloys Part II.—Alloys Rich in Aluminum, *J. Inst. Met.*, Vol. 65, 1939, p.403-418.
20. D. J. Sordélet, M. J. Kramer and O. Unal, Effect of Starting Powders on Controlling Microstructural Development of Al-Cu-Fe Quasicrystalline Plasma Sprayed Coatings, *J. Thermal Spray Tech.*, in press 1995.

21. E. Kubel, Jr., Powders Dictate Thermal Spray Coating Properties, *Adv. Mater. Proc.*, Vol. 138, 1990, p.24-26.
22. D. Tu, S. Chang, C. Chao and C. Lin, Tungsten Carbide Phase Transformation During the Plasma Spray Process, *J. Voc. Sci. Technol.*, Vol. A3, 1985, p. 2479-2482.
23. M. E. Vinayo, F. Kassobji, J. Guyonnet and P. Fauchais, Plasma Sprayed WC-Co Coatings: Influence of Spray Conditions (Atmospheric and Low Pressure Plasma Spraying) on the Crystal Structure, Porosity and Hardness, *J. Voc. Sci. Technol.*, Vol. A3, 1985, p.2482-2489.
24. R. A. Neiser, *Structure-Processing-Property Relationships in Air Plasma Sprayed $YBa_2Cu_3O_{7-\delta}$* , Ph.D. Thesis, State University of New York at Stony Brook, Department of Materials Science and Engineering, Stony Brook, NY, 1987.
25. D. J. Sordellet and J. E. Shield, Ames Laboratory, Iowa State University, unpublished research.
26. *Metals Handbook*, Desk Edition, Eds. H. E. Boyer and T. C. Gall, American Society for Metals, Metals Park, OH, 1985, p. 1-54.
27. S. Sampath and S. F. Wayne, *Plasma Sprayed Mo-Mo₂ C Composites: Microstructure and Properties*, in *Thermal Spray Coatings: Research, Design and Applications*, Eds. C. C. Berndt and T. F. Becnecki, ASM International, Materials Park, OH, 1993, p. 397-403.
28. D. J. Sordellet, P. D. Krotz, R. L. Daniels, Jr. and M. F. Smith, Microstructure and Wear Behavior of Quasicrystalline Thermal Spray Coatings, Proceedings of the 1995 National Thermal Spray Conference, in press 1995.
29. R. A. Neiser, private communication.
30. T. Yoshida and K. Akashi, Particle Heating in a Radio-Frequency Plasma Touch, *J. Appl. Phys.*, Vol. 48, 1977, p. 2252-2260.
31. J. M. Dubois and P. Weinland, U.S. Patent 5,204,191, April 1993.

32. J. L. Cohn, S. A. Wolf, T. A. Vanderah, V. Slevamanickam and K. Salama, Lattice Thermal Conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, *Physica C*, Vol. 192, 1992, p. 435-442.
33. R. Darolia, NiAl alloys for High-Temperature Structural Applications, *JOM*, 1991, p. 44-48.

CHAPTER 4:
EFFECTS OF BORON ON THE SOLIDIFICATION STRUCTURE
OF AN Al-Cu-Fe ALLOY

A letter to be submitted to the *Journal of Materials Science*

D. J. Sordélet, T. A. Bloomer, M. J. Kramer, and O. Unal

Ames Laboratory, U. S. DOE, Iowa State University

Ames, IA 50011

Additions of non-transition metals to modify the structure and stability of quasicrystalline phases have mostly been directed toward Al-Mn alloys [1-3]. Since the discovery of a stable icosahedral phase in Al-Cu-Fe alloys [4], work has been performed with this system to study the effects of transition and non-transition metal additions on solidified structures [5]. A recent study has examined the role of B substitutions for Al on the structure and stability of the icosahedral phase in Al-Cu-Fe melt spun ribbons [6]. The objective of this letter is to characterize the effect of adding B to Al-Cu-Fe materials prepared by chill casting, high pressure gas atomization and plasma arc spraying.

The alloy compositions used in this study were ternary $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and quaternary $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$. A chill cast ingot (CC) was prepared by bottom pouring the molten alloys into a water-cooled copper mold (5 cm dia. by 25 cm deep). A portion of the cast ingot was crushed into powder for subsequent characterization. The high pressure gas atomized powder (GA) was prepared under peak disintegration conditions with argon gas and approximately 250°C of superheat [7]. The parameters used to form the plasma arc sprayed coatings (PS) have been described elsewhere [8].

Powders and coatings were characterized with the following methods: X-ray powder diffraction (XRD) with $\text{CuK}\alpha$ radiation, differential thermal analysis (DTA) at a 10°C/min. scan rate in flowing argon, scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning Auger electron microscopy (SAM) and electron energy loss spectroscopy (EELS). Inductively-coupled plasma-atomic emission spectroscopy was used to verify that the GA powders were of the desired compositions (e.g., $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$).

The most dramatic effect of substituting 1 at. pct. of B for 1 at. pct. Al was seen in the solidification structure of the CC ingot. Figure 1 shows regions around the circumference and near the center of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ ingots. The phases in Figure 1 are predominantly monoclinic (λ), cubic (β) and icosahedral (ψ); these phases have been discussed

Figure 1. SEM micrographs from polished cross sections of chill cast ingots. Outer diameter of (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$, and center region of (c) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (d) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$.

(a)

(b)

(c)

(d)

in more detail previously by the authors [8]. From the backscattered electron images in Figure 1, it appears that similar phases are present in both ingots, but the scale of segregation and dendrite size of the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ ingot are much smaller. In addition, grains of a fourth phase on the order of $1\text{ }\mu\text{m}$ are visible in the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ ingot; these were identified with SAM to be $(\text{Al,Cu})\text{B}_2$, as discussed later. Both alloys exhibit coarser structures at the center of the ingots, which is expected due to cooling rate gradients. The similar phase assemblages of the two CC alloys were further observed using XRD (Figure 2). The patterns show mostly the icosahedral and cubic phases normally seen in this alloy [8]; some minor peaks from monoclinic and tetragonal (θ) phases are also present. Note, the θ phase is present in both alloys and is not the $(\text{Al,Cu})\text{B}_2$ phase mentioned above.

Backscattered SEM images from polished cross sections of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ GA powders (Fig. 3) show a mixed dendritic and cellular microstructure resulting from the rapid solidification rate during atomization. Powders between 5 and $100\text{ }\mu\text{m}$ were examined; a trend towards more dendritic growth was seen with increasing particle size in both samples. The SEM images in Figure 3 do not show a dramatic difference between the structures of the two powders. However, probing the structures on a finer scale with TEM clearly illustrates that adding B alters the microstructure of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ GA powders. The grain structures of 45 to $75\text{ }\mu\text{m}$ GA powders are presented in Figure 4. The dark and light phases seen in Figure 3 were identified by electron diffraction on the TEM to be the icosahedral and cubic structures, respectively. The microstructure of the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder (Fig. 4a) is characterized by well-faceted grains of the icosahedral phase surrounded by a matrix of the crystalline cubic phase. These results are consistent with TEM studies of gas atomized $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ powders [9]. In contrast, the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ powder does not exhibit the same faceted icosahedral grains, nor does it appear to have the same uniform matrix phase (Fig. 4b). The region of the ion-milled $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ sample shown in Figure 4b was relatively thick.

Figure 2. XRD patterns from (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ powder from crushed ingots.

Figure 3. SEM micrographs of polished cross sections of (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ gas atomized powders.

(a)

(b)

Figure 4. TEM bright field images of (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ gas atomized powders. In (b) small, dark areas are crystalline grains, while the large, light gray region is an icosahedral grain.

(a)

(b)

As a result, several crystalline grains were imaged along with a larger icosahedral grain through the foil thickness. Numerous icosahedral grains were examined, but none were seen which exhibited that same well-defined faceted morphology observed in Figure 4a. Grains of the monoclinic phase were seen in the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ powder, but not in the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder. This is likely due to the small regions which were sampled. Numerous λ grains were observed in the $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ study mentioned above [9]. X-ray diffraction patterns from the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ atomized powders were similar to each other and displayed mostly the ψ and β phases. No reflections from the λ phase were observed; however, the low symmetry of the monoclinic phase inhibits detection by XRD when it is present as a minor constituent.

The GA powders were used as feedstock to deposit PS coatings onto thin (0.5 mm) Al substrates. The coatings were core drilled and polished for TEM. The PS coatings are comprised of the same phases as the starting GA powders, as determined by XRD. Figure 5 displays representative TEM images from the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ coatings. Very small crystalline and quasicrystalline grains were seen throughout the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ coating. Several grains were detected (Fig. 5b) and analyzed by EELS to contain Al and B; however, no diffraction patterns were obtained to determine their structure. Examination of the limited areas which were sufficiently thinned during ion milling indicates that, in general, the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ PS coating has a slightly smaller average grain size; however, additional areas must be examined to better support this observation. More extensive TEM examination is also needed to make any general observations comparing ψ -phase facet formation in the two PS coatings.

Since the phase assemblages as determined by XRD of the CC and GA powders with and without B were similar, the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ CC and GA powders were vacuum annealed at 700°C for two hours in an attempt to identify any residual B-rich phases. The XRD patterns in Figure 6 show that both powders formed nearly single-phase icosahedral structures during

Figure 5. TEM bright field images of (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ plasma arc sprayed coatings. Area between arrows in (b) is an example of a large B-rich precipitate.

(a)

(b)

Figure 6. XRD patterns from vacuum annealed $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ (a) crushed chill cast ingot and (b) gas atomized powders.

annealing. There was no evidence of B-containing compounds (e.g., FeB or AlB₂). The low concentration of B in the alloy, however, would make identification of B compound difficult using only XRD. Accordingly, DTA was used to look for a phase difference between the two compositions of both CC and GA powders. Figures 7 and 8 show the thermal events during heating and cooling of the CC and GA powders, respectively. Clearly, there is an additional phase in the Al₆₂Cu₂₅Fe₁₂B alloys. During heating, this is evidenced by the endothermic peak around 800°C. Upon cooling, the solidification exotherm apparently from the additional phase is seen at a slightly lower temperature. The differences between the CC and GA DTA curves can be explained by the contrasting solidification structures seen in Figure 1, i.e., phase and chemical homogeneity differences. Close inspection of the DTA traces suggests that the addition of B alters the solidification kinetics of the alloys. The first exothermic solidification peaks around 960°C for both the Al₆₃Cu₂₅Fe₁₂ CC and GA powders are well-defined and narrow. However, the Al₆₂Cu₂₅Fe₁₂B CC and GA powders show broader peaks during primary crystallization. This observation is less pronounced during the subsequent solidification exotherms observed during cooling.

Boron is well known to facilitate grain refinement in Al alloys. Most often, the grain refinement mechanism involves either the precipitation of higher melting temperature B compounds, which act as heterogeneous nucleation sites [10], or the precipitation of primary crystallites or other intermetallic compounds which react peritectically with Al [11]. These processes, however, would produce thermal events during DTA at temperatures which are higher than the final melting of the Al₆₂Cu₂₅Fe₁₂B alloy. In the current study, the phase unique to the Al₆₂Cu₂₅Fe₁₂B alloy has a freezing temperature below the other phases, i.e., λ , β or ψ . This implies that B is continually being transported in the melt ahead of the moving solid-liquid interface after the primary phases have formed. Ultimately, B precipitates after the other phases have formed. This type of solute migration would cause B to be present at grain boundaries [12]. Figure 9 shows a fracture surface of the Al₆₂Cu₂₅Fe₁₂B cast ingot; fracture

Figure 7. DTA thermograms obtained during heating and cooling (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ powders from chill cast ingot.

Figure 8. DTA thermograms obtained during heating and cooling (a) $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and (b) $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ gas atomized powders.

Figure 9. SEM micrograph of fracture surface of $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ chill cast ingot. Features marked by arrows appear to be grain boundary particles or sites where grain boundary particles were removed along this apparent grain boundary.

occurred under vacuum in the SAM. The features marked by arrows appear to be individual grain boundary phase particles or sites where grain boundary particles were removed along this apparent grain boundary. Boron was detected in the locations of these particles by SAM. Polished cross sections (Fig. 10) were also examined by SAM and were found to contain numerous grains of about the same size as those in Figure 9. The auger lines detected from the dark phases in Figure 10 were from B, Al and Cu. Semi-quantitative analysis using peak-to-peak intensities yielded a general composition of $(\text{Al,Cu})\text{B}_2$; Cu was a minor constituent. The binary AlB_2 phase has a eutectic with Al around 655°C and melts peritectically near 980°C to form AlB_{12} and liquid. The unique phase in the $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ alloy (Figs. 7 and 8) melts within this temperature range, suggesting that the phase is approximately AlB_2 . Substitution of Cu for Al in this phase, as suggested by the SAM analysis, may lower the melting temperature to that observed. The complex multiple phase solidification structures formed in Al-Cu-Fe alloys preclude making further conclusions based on the limited data presented here.

The constant absorption of solute atoms by migrating boundaries significantly affects recrystallization, grain growth and phase transformation kinetics in metals [13] and ceramics [14]. Boron has been shown to segregate to grain boundaries in fcc Fe and bcc Fe-3%Si alloys [15, 16]. In the above examples, however, B is a condensed grain boundary phase which alters solid state reactions. In the current study, B appears to affect the solidification structure while it is still present as a solute in the liquid phase. Boron could be changing the viscosity of the melt and modifying growth kinetics. Also, continued rejection of B out of the solid-liquid interface into the melt would change the composition of the remaining liquid. These suggested mechanisms by which B alters the solidification structures are speculative. An assumption has been made that all of the B is indeed being carried along in the liquid and precipitating at grain boundaries. It is also possible that a portion of the B becomes incorporated into the solidified λ , β or ψ phases, but solubility limits force the remaining solute

Figure 10. SEM micrograph of polished cross section of $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ chill cast ingot. Dark regions are B-containing phases.

into the residual liquid. Further work is needed to better understand the role of B on altering the solidification of Al-Cu-Fe alloys.

A small addition of B (1 at. pct.) to an $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ alloy produced different solidification structures in chill cast ingots. The same primary phases formed, but dendrites and secondary arms were smaller and less faceted. Chemical segregation was less pronounced in the cast B-containing alloy. Microstructural differences between the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ and $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}\text{B}$ alloys were more subtle in powders formed by high pressure gas atomization or in coatings formed by plasma arc spraying. Nevertheless, TEM results of the GA powders and PS coatings clearly show a difference in grain structure between the two compositions. It appears that B is affecting the solidification morphology while it is present as a solute in the liquid rather than as a heterogeneous nucleant.

Acknowledgments

This study was performed at Ames Laboratory, Iowa State University, and was supported by the Director of Energy Research, Office of Basic Energy Sciences, United States Department of Energy under contract No. 2-7405-ENG-82.

References

1. S. NASNOA, W. DMOWSKI, T. EGAMI, J. W. RICHARDSON JR., and J. D. JORGENSEN, *Phys. Rev. B* **35** (1987) 435.
2. R. A. DUNLAP and V. SRINIVAS, *Phys. Rev. B* **40** (1989) 704.
3. P. A. HEINEY, P. A. BANCEL, A. I. GOLDMAN, and P. W. STEPHENS, *Phys. Rev. B* **34** (1986) 6746.
4. A. P. TSAI, A. INOUE, and T. MASUMOTO, *Jpn. J. Appl. Phys.* **26** (1987) L1505.
5. A. P. TSAI, A. INOUE, and T. MASUMOTO, *J. Mater. Sci. Lett.* **8** (1989) 470.
6. S. Y. HUANG and J. E. SHIELD, *Inter. J. Modern Phys.*, in press (1995).

7. I. E. ANDERSON , R.S. FIGIOLA and H. MORTON, *Materials Science and Engineering A*148 (1991) 101.
8. D. J. SORDELET, M. J. KRAMER and O. UNAL, *J. Thermal Spray Tech.*, in press (1995).
9. P. LIU, A. P. TSAI, A. INOUE, L. ARNBERG, *J. Mater. Sci.* **26** (1991) 963.
10. A. CIBULA, *J. Inst. Metals* **76** (1949-50) 321.
11. H. J. SEEMANN and H. STAATS, *Z. Metallk.* **59** (1968) 347.
12. X. L. HE, Y. Y. CHU and Z. S. YU, *Acta Metall. Sinica* **13** (1977) 225.
13. M. B. KASEN, *Acta Metall.* **31** (1983) 489.
14. W. C. JOHNSON, *Met. Trans. A* **8A** (1977) 1413.
15. X. L. HE, M. DJAHAZI, J. J. JONAS and, *Acta Metall. Mater.* **39** (1991) 2905.
16. S. ZHANG, X. LE, Y. CHU and T. KO, *J. Mater. Sci.* **29** (1994) 2655.

CHAPTER 5:
MICROSTRUCTURAL EVOLUTION, OXIDATION AND WEAR OF Al-Cu-Fe
QUASICRYSTALLINE COATINGS

A paper accepted by the *International Journal of Modern Physics*

D. J. Sordélet, M. J. Kramer, I. E. Anderson and M. F. Besser

Ames Laboratory, U. S. DOE, Iowa State University

Ames, IA 50011

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.

1. 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.

2. Experimental Procedure

2.1 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.

2.2 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, 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*.

2.3 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 CuK α 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 Al₆₃Cu₂₅Fe₁₂ 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 $1 \times 1 \times 10 \text{ mm}$ bars cut from sprayed coatings. Two bars from each coating were ground and polished to a $9 \mu\text{m}$ 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 $+53, -63 \mu\text{m}$ 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 $9 \mu\text{m}$ 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.

3. 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 $50\text{-}100 \mu\text{m}$. Since the ingot was crushed into particles ranging from 25 to $75 \mu\text{m}$, 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 (Figure 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 (Figure 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.

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

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

(a)

(b)

(c)

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

(a)

(b)

(c)

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

(a)

(b)

(c)

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

(a)

(b)

(c)

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*.

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 ($^{\circ}\text{C}$)	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.

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.

3.1 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 (Figure 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 (Figure 3c). The *Gca* coatings do not show the same splat boundary features, but do exhibit similar features in areas which contained unmelted particles (Figure 4b). The broad inhomogeneities of the *Cfa* and *Cca*

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 . Note that the vacuum annealed Gca coating which was oxidized in a continuous measurement experiment is included for comparison.

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 XRD results clearly show a phase evolution of the as-sprayed coatings during the 500°C oxidation tests (Figure 5). The two-theta values of individual XRD patterns were shifted using the ψ peaks as an internal standard. 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 (Figure 4c). Chemical analysis by EMP of the three phases in the 700°C oxidized *Gca* coating shows that the matrix is $\text{Al}_{62}\text{Cu}_{25}\text{Fe}_{12}$, 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 system⁷. 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 (Figure 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 (Figure 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.

3.2 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 (Figure 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 (Figure 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 appears that cracks formed and grew until large areas of material within the wear track were removed. At higher temperatures, the coating material

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 ceramic pins from (c) 25°C wear test and (d) 600°C wear test.

(a)

(b)

(c)

(d)

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 (Figure 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 Al_2O_3 pin surface (Figure 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.

4. Conclusion

Plasma arc sprayed $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ 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 μm 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 O_2 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 Al_2O_3 pin sliding against an $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ 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.

Acknowledgments

This study was performed at the Ames Laboratory, Iowa State University and was supported by the Director of Energy Research, Office of Basic Energy Sciences, United States Department of Energy under contract No. W-7405-ENG-82.

References

1. D. Shechtman, I. Blech, D. Gratias and J. W. Cahn, *Phys. Rev. Lett.* **53** (1984) 1951.
2. A. I. Goldman and M. Widom, *Ann. Rev. Phys. Chem.* **42** (1991) 685.
3. A. P. Tsai, A. Inoue and T. Masumoto, *Jpn. J. Appl. Phys.* **26** (1987) L1505.
4. J. M. Dubois, S. S. Kang and Y. Massiani, *J. Non-Cryst. Solids* **153 & 154** (1993) 443.
5. J. M. Dubois, A. Proner, B. Bucaille, Ph. Cathonnet, C. Dong, V. Richard, A. Piarelli, Y. Massiani, S. Alt-Yaazza and E. Belin-Ferre, *Ann. Chim. Fr.* **19** (1994) 3.
6. D. J. Sordet, M. J. Kramer and O. Unal, *J. Thermal Spray Tech.*, in press.
7. F. W. Gayle, A. J. Shapiro, F. S. Biancaniello and W. J. Boettinger, *Met. Trans. A* **23A** (1992) 2409.
8. A. J. Bradley and H. J. Goldschmidt, *J. Inst. Met.* **65** (1939) 389.
9. J. M. Dubois, S. S. Kang and J. Von Stebut, *J. Mater. Sci. Lett.* **10** (1991) 537.
10. R. H. J. Hannink, *Wear* **100** (1984) 355.

CHAPTER 6:
MICROSTRUCTURE AND WEAR BEHAVIOR
OF QUASICRYSTALLINE THERMAL SPRAYED COATINGS

A paper accepted for publication in the
Proceedings of the National Thermal Spray Conference,
September 1995, Houston, TX

D. J. Sordelet¹, P. D. Krotz², R. L. Daniel, Jr.² and M. F. Smith³

¹Ames Laboratory, U. S. DOE, Iowa State University
Ames, IA 50011

²Rockwell Aerospace, Huntsville, AL

³Sandia National Laboratories, Albuquerque, NM

Abstract

An Al-Cu-Fe alloy coating which forms a quasicrystalline phase is a potential candidate for replacing electro-deposited chromium on various components in the Space Shuttle Main Engine. Coatings were deposited by air and vacuum plasma spraying and by high-velocity oxygen-fuel spraying. Finer starting powders tended to lose Al during spraying, which affected the phase equilibrium of the coatings. Coatings which retained the starting powder composition were richer in the desired quasicrystalline phase. Ball-on-disk wear tests between 440C stainless steel ball and the Al-Cu-Fe coatings were performed. Coefficients of friction ranged from 0.60 to 1.2 for the different coatings.

1. Introduction

Thermal spray coatings are being developed for hardfacing and wear applications on the Space Shuttle's Main Engine (SSME) as replacements for electro-deposited (ED) chromium. Environmental regulations have imposed tight restrictions on ED processes to deposit chromium because of the associated release of hexavalent chromium (Cr^{6+}), which is a known human carcinogen. Specific coating systems and thermal spray techniques are being selected for individual SSME components, such as motor shafts and impellers, bearing supports and spacers and manifold assemblies.

A candidate coating material for high-wear applications is an Al-Cu-Fe alloy which forms a quasicrystalline phase. The term quasicrystalline is used to describe a unique class of materials which exhibit previously forbidden rotational symmetries (e.g., five-fold rotation) and lack periodic translational order (1). Figure 1 displays a bright field transmission electron microscopy (TEM) image of a quasicrystalline grain from a gas atomized $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder particle. The inset selected area diffraction pattern (SADP) illustrates the five-fold rotational symmetry and the absence of translational periodicity. Recent studies have demonstrated that Al-Cu-Fe quasicrystalline materials have high hardness, particularly for an Al-based alloy, and low coefficients of friction in unlubricated sliding (2). In addition, the Al-Cu-Fe quasicrystals possess relatively high hardness-to-elastic modulus ratios, which may be viewed as the ability for elastic recovery in parallel with the inability to absorb impact energy under contact deformation (3).

Liquid-to-solid processing of Al-Cu-Fe alloys by conventional methods such as casting, gas atomization, melt spinning and thermal spraying generally results in a mixture of ternary crystalline phases along with the quasicrystalline phase. The composition of the quasicrystalline phase (ψ) studied in this work was $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$, which has equilibrium relationships with a cubic (β) phase and a monoclinic (λ) phase (4). These phases will be referred to throughout the text.

Figure 1. Bright field TEM image of a quasicrystalline grain from a gas atomized powder particle.

Several studies discuss the effect of starting powders on the structure of plasma sprayed Al-Cu-Fe coatings (5,6). However, very little data exist on relating the structure and chemistry of quasicrystalline coatings to their physical properties. The objectives of this work were to characterize the microstructure of Al-Cu-Fe thermal sprayed coatings and to observe their tribological behavior during ball-on-disc wear testing.

2. Methods and Materials

2.1 Thermal Spray Coatings

Coatings were deposited using atmospheric plasma spraying (APS), vacuum plasma spraying (VPS) and high-velocity oxygen-fuel spraying (HVOF). Table 1 lists the operating parameters used with the three coating methods. Starting powders with a nominal composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ were prepared by gas atomization. Characterization of these powders has been discussed elsewhere (5). The gas atomized powders were screened to below 45 μm , and then further separated into +25, -45 μm and -25 μm size fractions. The coatings prepared in this study are described in Table 2.

2.2 Microstructural Characterization

The compositions of the starting powder and the different coatings were determined using atomic emission spectroscopy. Bulk oxygen contents were measured with inert gas fusion. Structural analysis was carried out using X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation. Microstructures of powders and coatings were observed with scanning electron microscopy (SEM). Indentation hardness measurements were made with a Vickers indenter under a 30g load. At least ten measurements were taken and averaged from each coating.

Table 1. Thermal Spraying Parameters

Parameter	Thermal Spray Process		
	APS	VPS	HVOF
Gun	SG-100*	SG-100*	JP-5000
Chamber Pressure (torr)		200 (Ar)	
Anode (part number)	358	730	
Cathode (part number)	112	720	
Gas Injector (part number)	113	112	
Current (amperes)	800	610	
Voltage (volts)	43.6	41	
Arc gas (slpm)	37.8 (Ar)	73 (Ar)	
Aux gas (slpm)	20.0 (He)	5.6 (H ₂)	
Kerosene flow rate (@0.76MPa) (slpm)			0.42
Oxygen flow rate (@0.78MPa) (slpm)			776
Carrier gas (slpm)	5.6	4.7	2.1
Powder feed rate (g/min)	20.0	13.5	34
Stand off (cm)	7.5	17.5	38

*Miller Thermal, Hobart Tafa

2.3 Ball-on-disk testing

Disks were 440C stainless steel, which were coated with the Al₆₃Cu₂₅Fe₁₂ powder using APS, VPS and HVOF. The coatings were polished to a 0.1 µm finish before testing. The ball was also 440C stainless steel. A 250 g load was applied to the 12.7 mm diameter ball. Tests were performed at room temperature with a linear velocity of 2.5 cm/s. The testing materials, geometries and loading conditions produced an estimated contact pressure of 0.36 GPa. Coefficient of friction data was recorded as a function of sliding distance.

3. Results and Discussion

3.1 Coating characterization

The gas atomized powder used in this study is shown in Figure 2. Chemical analysis of the powder revealed that the composition was Al₆₃Cu₂₅Fe₁₂; the starting powders contained

about 0.11 w/o O. The compositions of the as-sprayed coatings are given in Table 2. The first APS coating (AP1) and VPS coating (VP1) were prepared with -45 μm and -25 μm size fraction powders, respectively. It appears that the spraying parameters used with these size fractions were too aggressive. The AP1 and VP1 coatings lost Al during spraying. This chemistry change moves the coating composition away from a single-phase ψ region in the Al-Cu-Fe phase diagram (7). The result of this composition change can be seen in the XRD patterns of the AP1 and VP1 coatings compared to the starting powder (Figure 3b,3d). The relative fraction of the desired ψ phase compared to the β phase is much higher in the starting powder than in the AP1 or VP1 coatings.

Table 2. Chemical Analysis of Thermal Sprayed Coatings

Coating Label	Thermal Spray Process	Starting Powder Size (μm)	Chemical Analysis*			
			Al (w/o)	Cu (w/o)	Fe (w/o)	O (w/o)
AP1	Atmospheric Plasma Spray	-45	38.4	40.2	17.4	1.2
AP2	Atmospheric Plasma Spray	+25, -45	40.0	40.7	16.9	0.8
VP1	Vacuum Plasma Spray	-25	37.7	39.3	17.5	0.3
VP2	Vacuum Plasma Spray	+25, -45	42.2	39.7	17.1	0.3
HVO	High Velocity Oxygen Fuel Spray	-45	41.7	40.4	16.8	0.8

*Composition of $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ in w/o is approximately 42.3% Al, 40.0% Cu, 17.7% Fe.

A coarser cut of powder between 25 and 45 μm was used to form additional atmospheric and vacuum plasma sprayed coatings (AP2 and VP2). The coarser particles did not lose as much Al during spraying (Table 2). Again, this effect is seen in the XRD patterns of the AP2 and VP2 coatings formed with the coarser size fraction powders (Figure 3c,e). The AP2 coating still lost some Al during deposition, but not as much as the AP1 coating. The

Figure 2. SEM micrograph of -45 μm gas atomized $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powders.

Figure 3. XRD patterns of gas atomized starting powder and thermal sprayed coatings, as follows: (a) starting powder; (b) AP1; (c) AP2; (d) VP1; (e) VP2; and (f) HVO.

reduced material loss of the AP2 coating corresponds with a relatively higher ψ phase fraction in the coating. The VP2 coating is clearly much richer in the ψ phase than the VP1 coating. This is likely due to a combination of chemistry and substrate temperature effects.

The +25, -45 μm powder did not lose much Al during deposition; furthermore, the temperature of the substrate during coating was around 450°C. The ψ phase is thermodynamically stable at elevated temperatures, so it is possible that some degree of phase homogenization occurred during spraying (7).

The parameters used during HVOF spraying did not produce the chemistry changes seen with the two plasma spraying methods (Table 2). Compared to the AP2 coating, the HVO coating lost slightly less Al during spraying, and shows a higher corresponding fraction of the ψ phase (Figure 3f).

SEM images of polished cross sections of the APS coatings are displayed in Figure 4. These coatings show some large pores and many cracks along splat boundaries. The AP2 coating tended to exhibit more cracking through splats parallel to the spraying direction. This may be due to the larger average particle size of the powder used to form the AP2 coatings. The ψ and β phase have low fracture toughness values (8), which makes thicker splats more prone to cracking.

The VPS coatings are denser than the APS coatings (Figure 5). The VP1 coating has a small volume of porosity, but does not show the same degree of cracking as the APS coatings. The VP2 coating is very dense towards the as-sprayed surface. However, although not pictured here, there is a band of coating approximately 100 μm thick along the substrate interface which is much more porous than the area displayed in Figure 5b. The VP1 coating does not have the same porous band along the substrate. Since all the coatings were ground and polished at the same time, it does not appear that the porous layer in the VP2 coating is an artifact of the metallographic process.

Figure 4. SEM micrographs (backscattered electrons) of APS coatings (a) AP1 and (b) AP2.

(a)

(b)

Figure 5. SEM micrographs (backscattered electrons) of VPS coatings (a) VP1 and (b) VP2.

(a)

(b)

The coating deposited by HVOF (Figure 6) has several characteristics common to the APS coatings. There are pores and cracks in the HVO coating. In addition, it appears that some localized oxidation occurred during HVOF spraying. The sample region shown in Figure 6 has several bright areas. Qualitative energy dispersive spectroscopy indicated that the bright areas are higher in Cu and Fe than the surrounding matrix. There are also some dark regions, which are generally adjacent to the bright regions, that are richer in Al than the surrounding matrix. It is likely that isolated surface oxidation during spraying consumed Al to form Al_2O_3 and left neighboring areas relatively more concentrated in Cu and Fe. The bulk oxygen values of the AP1, AP2, and HVO coatings are similar (Table 2), however the APS coatings did not exhibit the same localized elemental segregation as the HVO coating.

Table 3 lists the average indentation hardness measurements ($\pm$ one standard deviation) obtained from the APS, VPS and HVOF coatings. The higher densities of the VPS coatings are associated with higher hardness values. It is not clear why the AP1 coatings have an higher average hardness than the AP2 coatings despite being leaner in the harder quasicrystalline Ψ phase. Furthermore, there is no evidence to suggest why the HVO coating has a lower hardness. With the small 30 g load, the indents in the coating are larger than the localized areas of elemental segregation discussed above. The large scatter in the data precludes further speculation between coating hardness values.

Table 3. Indentation Hardness Results

Coating	Hardness ($\text{HV}_{0.03}$)
AP1	876 ± 74
AP2	773 ± 154
VP1	803 ± 161
VP2	876 ± 144
HVO	610 ± 80

Figure 6. SEM micrograph (backscattered electrons) of HVOF coating HVO.

0076 10KV X500 10 μ m WD27

3.2 Wear Testing

The wear behavior of the thermal spray coatings appears to be more sensitive to coating density and topography than to phase chemistry. Plots of coefficients of friction as a function of sliding distance obtained from the different coatings are shown in Figure 7. The data presented are filtered averages from the raw data. The APS coatings (Figure 7a) produced very similar wear-in and steady state behavior despite being comprised of different fractions of ψ and β phases (Figure 3b,c). The two VPS coatings exhibited comparable initial wear-in behavior but the VP2 coating increased to a higher coefficient of friction before leveling off to a nearly steady state condition. Note that the test with VP2 coating was terminated after approximately 30 m of sliding. The HVO coating had a much slower wear-in transition period (Figure 7c). The coefficient of friction increased slightly throughout the test to a value greater than 1.0.

The variability between the VPS and APS coatings is likely due to the surface finish created as a result of the spray parameters and the starting powder. In comparing optical photographs of the polished plasma sprayed coatings, it was seen that the surfaces had a "mud cracking" appearance (Figure 8). The scale of the cracking pattern was smaller with the AP1 and VP1 coatings, which were sprayed with finer powders. On the other hand, the HVO coating did not exhibit the same as-polished surface cracks. This may be due to the lower hardness of the HVO coating or to contrasting compressive/tensile stress states. HVOF deposition tends to produce coatings with less residual stress, because the high impact velocities of the spray particles have an effect similar to peening of the surface, (i.e., the impacts tend to relieve tensile surface stress and may induce compressive stress at the surface). The higher porosity and cracking in the APS coatings would be expected to produce a lower bearing surface area than the VPS or HVOF coatings. Since frictional force can be approximated as the product of surface area and shear force (9), the reduced contact area between the ball and the polished APS coatings corresponds to a lower coefficient of friction.

Figure 7. Coefficient of friction versus sliding distance for (a) APS, (b) VPS, and (c) HVOF thermal spray coatings.

Figure 8. Optical micrographs of polished (a) HVO and (b) VP2 coatings on test rings.

(a)

(b)

The slightly higher coefficient of friction in of the VP2 coating compared to the VP1 coating may also result from the slight density and concomitant contact area differences between the two coatings. The lower hardness of the HVO coating may be associated with a higher coefficient of friction since a larger contact area between the ball and polished coating would be generated during sliding. Also, the as-sprayed HVO coating was on approximately 100 μm thick. If the coating thickness was reduced substantially during polishing, then there may have been a contribution to the wear behavior from the softer substrate during testing. Dubois, et al. detected substrate effects during scratch testing when the coating thickness was less than 60 μm (10). However, actual minimum thicknesses are very specific to coating properties and testing configurations.

The above discussion of the preliminary wear tests is quite speculative. Further testing is required in tandem with an analysis of wear surfaces to establish the relationships between coating microstructure and tribological behavior.

Acknowledgments

One author (DJS) would like to acknowledge the support of the Director of Energy Research through the Office of Energy Sciences, US Department of Energy under contract No. 2-7405-ENG-82.

References

1. Goldman, A. I. and M. Widom, *Annu. Rev. Phys. Chem.* 42, 685 (1991).
2. Dubois, J. M., S. S. Kang and J. Von Stebut, *J. Mater. Sci. Lett.* 10, 537 (1991).
3. Lawn, B. R. and V. R. Howes, *J. Mater. Sci.* 16, 2745 (1981).
4. Gratias, D., Y. Calvayrac, J. Devaud-Rzepski, F. Faudot, M. Harmelin, A. Quivy and P. A. Barcel, *J. Non-Cryst. Solids* 153 & 154, 482 (1993).
5. Sordelet, D. J., M. J. Kramer and O. Unal, *J. Thermal Spray Tech.*, in press.

6. Sordélet, D. J., M. J. Kramer, I. E. Anderson and M. F. Besser, Proceeding of the Fifth International Conference on Quasicrystals, May 1995, Avignon, France (World Scientific), in press.
7. Gayle, F. W., A. J. Shapiro, F. S. Biancaniello and W. J. Boettinger, Met. Trans. 23A, 2409 (1992).
8. Koster, U, W. Liu, H. Leibertz and M. Michel, J. Non-Cryst. Solids 153 & 154, 446 (1993).
9. I. M. Hutchings, "Tribology: Friction and Wear of Engineering Materials," p. 28, CRC Press, Boca Raton, Florida (1992).
10. Kang, S. S., J. M. Dubois, and J. von Stebut, J. Mater. Res. 8, 2471 (1993).

CHAPTER 7:

GENERAL CONCLUSION

Although a stable quasicrystalline phase exists in the Al-Cu-Fe system, it exists over a narrow composition range centered approximately around $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$. Furthermore, the quasicrystalline phase does not form directly upon solidification; it forms peritectically through reaction between liquid and higher melting temperature crystalline phases. The above characteristics make the synthesis of a single-phase quasicrystalline structure very difficult using traditional solidification processing techniques. The microstructures developed in $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ cast ingots and gas atomized powders were found to contain the quasicrystalline phase along with several crystalline phases. The cast ingots were highly segregated. It was observed, however, that small additions of B to the alloy reduced the inhomogeneity.

Understanding the chemistry and structure of cast ingots and gas atomized powder was essential for subsequent studies of plasma arc coatings. The cast ingots, which were crushed into powder, and the gas atomized powder were used as feedstock to form plasma arc sprayed coatings. The microstructure of the coatings was highly dependent on the chemical uniformity of the starting powders. The increased homogeneity of the gas atomized powder produced much more uniform coatings than the crushed powder obtained from cast ingots. The scale of segregation in the cast ingots was large enough to result in individual crushed powder particles (e.g. 10 - 100 μm) with different compositions and structures. Conversely, the gas atomized powders were extremely uniform. Since the buildup of a plasma sprayed coating is essentially an integration of individual solidification events, it is straightforward to envision how powder uniformity, particularly down to the scale of individual powder particles, impacts the ultimate coating uniformity.

Future studies to produce Al-Cu-Fe powders with higher quasicrystalline phase contents for plasma could involve adjusting compositions within the ternary system or adding

trace elements (e.g., B). However, it must be remembered that the plasma arc spraying process, if practiced correctly, melts the powders. Therefore, the starting powder solidification structure is lost during the plasma arc spraying process. This does not preclude obtaining coating structures which are similar to the starting powders. More importantly, it helps reinforce the necessity to thoroughly consider the processing of the starting powder as a key variable in forming plasma arc sprayed coatings.

The unusually low thermal conductivity of the quasicrystalline phase in the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ gas atomized powders caused problems during plasma arc spraying. Specifically, finer starting powder particle sizes tended to lose Al by vaporization during spraying. This shifted the composition of the molten particles away from the single phase quasicrystalline stability field and increased the fraction of the cubic phase in the sprayed coatings. This effect was not observed while spraying starting powders with coarser particle sizes (e.g., $>45\text{ }\mu\text{m}$). All these experiments were performed with the same plasma gun operating parameters. Therefore, there is not an inherent problem with spraying $\sim 45\text{ }\mu\text{m}$ $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ powder particles. Rather, these observations illustrate the critical need to develop plasma arc spraying conditions which provide sufficient thermal energy to the $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ particles to fully melt them, but does not overheat them to the point of particle vaporization.

Future work to refine coating process parameters with Al-Cu-Fe powders is necessary in light of the material's thermal properties, complex solidification and narrow phase field composition limits. Suggested studies would include statistically designed experiments evaluating thermal and kinetic energy transfer, gun-to-substrate distance and powder mass flow rates. Response variables of interest include phase constitution (e.g., v/o of quasicrystalline phase), coating density and coating hardness.

Quasicrystals in the Al-Cu-Fe system have been suggested to have interesting physical properties such as wear and corrosion resistance. Before the properties can be fully studied,

materials of known structures need to be processed. The survey of physical properties performed in this work showed that $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ plasma arc sprayed coatings are resistant to catastrophic oxidation at temperatures up to 700°C . However, concurrent with formation of a protective oxide film, evidence of decomposition of the quasicrystalline phase into crystalline phases was observed in the coating. This behavior is not only an academic curiosity, but may also have strong technological implications. Accordingly, future studies of single phase Al-Cu-Fe quasicrystalline materials (e.g., powders, coatings or bulk specimens) is necessary to elucidate the role of oxygen on phase stability at elevated temperatures. These experiments would be excellent complements to surface studies on single phase quasicrystalline and companion crystalline materials.

The wear behavior of the quasicrystalline coatings examined in this study was characteristic of many brittle intermetallic materials. The pin-on-disc tests were run using an Al_2O_3 pin with a hemispherical end. The hardness and geometry of the pin produced very high contact stresses; this was intentional in order to observe material damage during sliding. At room temperature, the quasicrystalline coatings were very brittle and produced finely-divided wear debris. At higher temperatures ($200 - 400^{\circ}\text{C}$), the coatings exhibited increased plastic deformation. The wear debris was more aggregated and adhered strongly to the Al_2O_3 pin. Friction coefficients increase with increased temperature and sliding distance. This was attributed to increased contact area between the pin and the quasicrystal coating.

One of the most promising applications of Al-Cu-Fe quasicrystals is as hard, wear-resistant, low-friction coatings. In this light, far more tribological evaluation is necessary to evaluate a range of variables, including sliding velocity, normal load, contact materials, and testing environment. A fundamental ultra-high vacuum friction study would be very desirable with quasicrystals. Sliding identical materials, or materials with similar crystal structure, against each other in a vacuum produces high frictional forces due in part to the adhesive energy of commensurate lattices, according to theory. The aperiodic arrangement of atoms in a

quasicrystal would inhibit this effect when two quasicrystal surfaces are brought into contact with each other. While many material properties affect frictional forces between two sliding bodies, the contribution from adhesive energy can be significant. The suggested tests would help address many of the hypotheses about the tribological behavior of quasicrystals.

In conclusion, the physical and chemical properties of Al-Cu-Fe quasicrystals offer interesting potential for both industrial applications and academic studies. Their complex phase equilibrium and solidification behavior, however, require a thoughtful, comprehensive approach in developing and refining processing techniques.