The effect of oxygen contamination on the amorphous structure of
thermally sprayed coatings of $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_8\text{Si}_1$

by

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Give your children books.

1. INTRODUCTION

1.1 Metallic glasses

Since the first report of a metallic system showing an amorphous structure¹, scientists have sought to explain the formation behavior and unique properties of these materials. Moreover, attempts have been made to utilize amorphous metallic alloys in applications currently filled by conventional crystalline metallic systems. In order to determine what constitutes a metallic glass system, the scientific community has drawn on the deep history and well-established nomenclature associated with common oxide glasses.

Amorphous material differs structurally from its crystalline counterparts in that they do not exhibit any long-range periodic order. Whereas a crystalline material exhibits repeating atomic arrangements that are uniform and predictable throughout the material, the random dense packing of atoms in amorphous samples is limited to atomic clusters that are generally similar in arrangement to what is found in the liquid of the same composition. This difference in structure is apparent when comparing general thermal, mechanical, and structural characteristics of metallic glasses, crystalline metallic systems, and oxide-glass systems as shown in Table 1.

Table 1. Comparison of typical characteristics of crystalline metals, oxide glasses, and metallic glasses.²

Property	Metal	Oxide Glass	Metallic Glass
Structure	Crystalline	Amorphous	Amorphous
Bonding	Metallic	Covalent	Metallic
Yield stress	Non-ideal	Almost ideal	Almost ideal
Workability	Good, ductile	Poor, brittle	Good, ductile
Hardness	Low to high	Very high	Very high
Ultimate tensile stress	Low to high	Low	High to very high
Optical transmission	Opaque	Transparent	Opaque
Thermal conductivity	Very good	Poor	Very good
Electrical resistance	Very low	High	Very low
Corrosion resistance	Poor to good	Very good	Very good
Magnetic properties	Various	Non-existent	Various

The formation of an amorphous structure from the liquid state is similar for metallic and non-metallic systems. The amorphous state is formed when the temperature of a melt is decreased from the liquidus temperature (T_m) to below the crystallization temperature (T_x), to the glass transition temperature (T_g). This cooling must be sufficiently rapid to avoid significant nucleation or growth of crystalline phases which occur inside the “nose” of the Time-Temperature-Transformation (TTT) diagram, as illustrated in Figure 1. Varying the cooling rate of an amorphous alloy can cause the glass transition to occur at different temperatures; lower cooling rates tend to lower T_g . The temperature range between T_g and T_x is known as ΔT_x and is an indicator of the stability of the amorphous structure. The occurrence of ΔT_x provides the opportunity for processing amorphous alloys using deformation processes such as warm extrusion where the alloy is heated sufficiently to lower the viscosity to a workable level (above T_g) but kept from crystallization (below T_x). This processing provides an exciting opportunity to fabricate useful geometries from these materials.

Figure 1. Schematic TTT diagram showing the critical cooling path required to avoid crystallization.

likely that similar compositions will also form a glass. If T_g is taken as constant over relatively small changes in composition, then T_{rg} will vary inversely with T_m and reach a local maximum where deep eutectics are found. The Turnbull relationship has indeed been found a good predictor of compositions that are potential glass forming metallic alloys. Further criteria, or general characteristics have subsequently been found in multi-component alloys that have very low $\dot{\tau}$ and can be formed in large cross-sections. These are discussed below.

$$T_{rg} = T_g / T_m \quad \text{Equation 1}$$

In addition to the Turnbull criterion, other predictors of glass-forming ability (GFA) are especially useful when dealing with higher-order alloys. Inoue has proposed a comprehensive flow chart summarizing these relationships as presented in Figure 3.¹⁰ These guidelines illustrate the mechanisms by which modern multi-component systems are capable of avoiding significant crystallization during solidification. As described earlier, a metastable amorphous phase is formed when the nucleation or growth of the crystalline phase is suppressed. Nucleation can be suppressed by the high solid/liquid interfacial energy due to local atomic arrangements in the liquid. Growth of nuclei formed either heterogeneously or homogeneously can be greatly limited by the long distances over which atoms must diffuse to form the crystalline lattice for complex alloy systems. Additionally, suppression of both nucleation and growth of crystalline phases is aided by increasing viscosity with decreasing temperature. By meeting Inoue's first condition of multiple typed/sized elements that resist mixing, the structures in amorphous alloys tend to form dense random-packed structures that increase viscosity, thereby reducing the diffusion necessary for crystallization. This reduction in diffusion is even more significant when coupled with the longer diffusion lengths required to form the crystalline phases found in these alloys.

Figure 3. Mechanisms for stabilization for glass-forming alloys.¹⁰

In order to study a metallic glass-forming system it is necessary to identify the atomic structures that are present. The determination of amorphous structure for many analytical techniques relies largely on the elimination of the presence of detectable crystalline structure. In a conventional alloy system, one of the most common techniques utilized for structure determination is X-ray diffraction (XRD). The diffracted intensity of the Bragg peaks results from differences in atomic packing density on planes of the crystal lattice. In amorphous systems there are no lattice or periodic structures to give sharp diffracted intensities. In contrast to the unique set of sharp peaks of a crystalline material (Figure 5a), an amorphous structure will exhibit only broad diffuse diffraction peaks (Figure 5b). These humps are an indication of the local atomic spacing found in the amorphous structure.¹² Since these distances are not fixed, no single 2θ value will correspond to the diffracted intensity for a specific atomic pairing.

amorphous systems, the minimum detectable amount of crystalline phase would be estimated at a few percent. In spite of the limitations of XRD, it is still a useful screening tool if used as a necessary, but not sufficient condition for the determination of the presence of amorphous material.

Figure 5. XRD plots of (a) crystalline diffraction and (b) amorphous diffraction.

Another method to examine the structure of an amorphous sample is to observe changes that occur in the material as it is heated. Differences in thermodynamic properties between the amorphous and crystalline structures can be detected as a function of temperature by using techniques such as differential scanning calorimetry (DSC) to observe changes in specific heat (C_p). Changes in C_p can indicate the occurrence of T_g , T_x , and T_m ; furthermore, DSC can give a semi-quantitative value to the enthalpy change during crystallization. This enthalpy change can be used to indicate the relative amount of crystalline phase present in the amorphous structure when compared to a sample of known phase purity. This comparison technique is explained in more detail later. Figure 6 shows a schematic drawing of a DSC thermogram illustrating the significance of the changes in C_p observed in a material cooled from a liquid to below T_g . The schematic thermogram shows the changes in C_p as a function of temperature on heating displaying the glass-transition as an endothermic event and the primary crystallization event as an exothermic event marking the occurrence of T_g and T_x respectively. In addition to changes in C_p , the glass transition is

1.2 Thermal spray

The liquid-to-solid processing technique chosen for this work is thermal spraying. Thermal spray is a generic name for a group of processes in which a feed material is melted and projected toward a substrate in order to form a surface coating. This coating can be as thin as a few microns or as thick as several centimeters depending on the material being sprayed and the technique being used. Almost any material that exhibits melting can be deposited via thermal spray. The characteristics of the coating can be modified based on controlling the interactions of the feed material during heating, flight, and deposition.

One method of thermal spray that has been shown to be useful for deposition of coatings of amorphous alloys is plasma arc spray (PAS). In PAS the heat for the process is provided by ionizing an inert gas, usually argon mixed with helium, and forming a thermal plasma which has been estimated to reach temperatures in the 15,000 - 30,000K range.¹⁴ Once a plasma is formed, the feed material, in powder form is entrained in a gas stream and injected into the plasma plume where it is heated. Kinetic energy is imparted to the molten material by the expanding arc gases and the droplets are propelled toward the substrate.

To summarize PAS, the sprayed material will interact with three regimes: the gun, which controls how the particle melts and the velocity of the molten particle, the surrounding atmosphere which affects particle temperature and reaction, and the substrate which affects solidification and cooling. A cross section of a typical plasma arc spray gun is presented in. The gun consists of two electrodes: a tungsten cathode that resides within a cylindrical copper anode. The process begins as an arc is struck between the two electrodes through the flowing arc gas. The gas evolves through a dissociation and ionization process, forming a plasma, which is stabilized by a low voltage, high current DC-source. The geometry of the copper anode forces the rapidly expanding gas to accelerate, and results in the formation of a high velocity, high temperature plasma. The coating material is introduced as a powder in a stream of argon carrier gas as shown in, or externally if it is desired to utilize a cooler region of the plasma. The particles are rapidly heated and accelerated from the gun where they strike the substrate to form a tenaciously bonded coating.

As the molten droplets arrive at the substrate they strike the surface and begin to spread out as they cool. The deposits adhere to the substrate almost exclusively by

quality of contact between splats, and splat thickness. Substrate temperature can be controlled to some extent by spray patterns, substrate material selection, and external cooling. Splat contact quality is often strongly affected by the oxidation of the molten feed material during flight. Higher oxide content reduces the heat flow between splats due to reduced thermal conductivity and decreased coating density. The cooling within a solidified splat is a function of the splat thickness. This thickness is largely dependent on the particle velocity and viscosity; with higher velocities leading to thinner splats that cool more quickly

Figure 8. Schematic of a thermal sprayed coating.¹⁴

In addition to spraying coatings in ambient atmosphere, it is common to plasma arc spray coatings in a controlled environment, usually a large vacuum chamber, known as vacuum plasma spray (VPS). Spraying coatings with atmospheric control can lead to improvements in coating quality. If the chamber is filled with an inert gas, such as Ar, it is possible to spray materials that are oxygen sensitive without significant oxidation. It is also possible to increase coating density by spraying at a reduced chamber pressure, typically ~300 Torr. The reduced pressure has two effects on the plasma spray process: 1) it can increase the plasma gas velocities which will increase the velocity of the entrained molten

are selected between 25 μm and 75 μm . Powders larger than this range are difficult to heat uniformly and resist acceleration in the plasma gasses. Below this limit, powders are difficult to feed into the gun smoothly and are often subject to overheating, which can cause material loss and oxidation.²²

1.3 Cavitation erosion

In addition to the chemical and structural characterization of the amorphous metallic coatings prepared in this work, a series of cavitation erosion tests were performed to look for a correlation between their structure and tribological behavior.

Cavitation erosion is a form of material damage that is found to occur in liquid environments. Surface damage due to the formation and collapse of vapor bubbles at or near the surface erodes the material causing part failure. Cavitation occurs in two modes: liquid droplet impingement and vapor bubble collapse. The former is typical of damage produced by raindrops impacting on aircraft skins or propeller blades, or in the cooler sections of steam turbines. The latter form of cavitation erosion is commonly found anywhere that there are rapid changes in fluid velocity, such as near an oscillating surface or sharp corners in fluid flow past a propeller, for example.

The forces that cause cavitation erosion damage are generated when a sudden pressure change in the fluid causes the formation of a vapor bubble at or near the solid-liquid interface. This bubble collapses, creating a liquid jet if the bubble occurred at the surface, or a shock wave if the bubble was near the surface. These events can exert great pressure upon a surface and impact stresses of 100 MPa - 10 GPa have been reported.^{23,24}

To resist the damage caused by cavitation, the energy from the bubble collapse must be absorbed by the material in a non-destructive manner. Ideal characteristics would be high strength and high elastic limit. It should follow that amorphous metals that exhibit tensile strengths of ~ 2 GPa and elastic strain limits of 2% should be ideal candidates when compared to crystalline intermetallic alloys that typically exhibit 0.5-1% elastic strain limits. Based on the calculation of elastic strain energy²⁵ in Equation 2, where E is Young's modulus, U is the elastic strain energy, and ϵ is strain; for the nearly perfect Hookean

Figure 9. Cavitation erosion as a function of fatigue strength coefficient and cyclic strain hardening.²⁸

Figure 10. Volume loss from cavitation erosion for common metals including bulk metallic glass.

of reducing the dwell time of the feed powder in the plasma, decreasing particle heating. The conditions chosen are typical of those used to spray materials prone to oxidation or vaporization during plasma arc spraying.²²

Table 3. Plasma arc spray gun configuration and parameters.

Gun Mode (SG-100)*	Mach I
Anode, part number*	358
Cathode, part number*	112
Gas injector, part number*	113
Amps	800
Arc Gas, slpm	37.8 (Ar)
Auxiliary gas, slpm	20.0 (He)
Carrier Gas, slpm	5.6 (Ar)
Powder feed rate, g/min	15
Stand-off, cm	Various

* Praxair Surface Technologies

For deposition of the vacuum plasma sprayed (VPS) coatings, the spray environment was controlled by use of a vacuum chamber to exclude atmospheric oxygen. The vacuum chamber is a stainless steel-walled, water-jacketed vessel with a capacity of approximately 2.8 m³. Evacuation is achieved by using a mechanical pump assisted by a roots-vane blower. Pressure within the chamber is controlled by actuation of a butterfly valve set to maintain a preset pressure of 40 kPa during spraying.

Samples were mounted in the spray fixture and the chamber was closed and evacuated to approximately 9.3 Pa, which is the lowest pressure attainable by this system. Upon reaching the low pressure limit the chamber was flushed with argon to 93 kPa, just below ambient pressure; followed by pumping again to 9.3 Pa before backfilling with argon to the spraying pressure of 40 kPa. Oxygen levels in this chamber are typically below 0.1%. When spraying in the chamber, the samples were cooled with a gun-mounted pair of gas jets directing argon toward the substrates. Following completion of the spray run the chamber was again evacuated for approximately 20 minutes to allow the samples and fixtures to cool prior to exposing them to air. This was done to prevent further oxidation of the coatings after spraying. Following the cool-down, the chamber was backfilled to atmosphere with argon.

function of spray distance for the APS samples is plotted in Figure 11. Note, the temperatures were measured at the stand-off distance specified.

Figure 11. Average particle temperature as a function of spray distance.

2.3 Characterization

Oxygen content was measured by inert-gas fusion, performed using a Leco TC-436 (St. Joseph, MI). Measurements were gathered from all starting powders and all coatings sprayed onto 1080 steel. Oxygen is reported as weight percent, while metals-basis chemistry analyses are reported in atomic percent.

Metals-basis chemical analysis was done by NSL Analytical Services, Inc. (Cleveland, OH). Inductively coupled plasma-atomic energy spectroscopy (ICP-AES) was used to measure the amounts of Ti, Zr, Cu, and Ni; while wet-chemistry was used for Si analysis. Chemical analysis was carried out on all starting powders, but only coatings from starting Powders *a*, and *e* were analyzed. The exclusion of samples made from Powders *b*, *c*,

In addition to chemical, X-ray, and thermal characterization, samples of all coatings were prepared for microscopy. Mounts were made by epoxy vacuum-impregnation followed by sawing using a diamond saw to expose an intact coating cross-section. The mounts were then polished with Buehler automated polishing equipment. All mounts were photographed using optical microscopy to screen for anomalous features. Samples of *aVI3* and *aAI3* were also observed using scanning electron microscopy (SEM). A Hitachi S2460-N low-vacuum SEM was used to obtain secondary (SE) and backscattered (BSE) electron images, as well as semi-quantitative energy dispersive spectroscopy (EDS). SEM observation was performed on an area of each selected coating that had been previously profiled for composition using electron-probe microanalysis (EPMA) with a data step size of 2 μm . Scanning Auger microscopy (SAM) was also used to examine and map chemical concentration for the cross-section of sample *eAI3* that was fractured in-situ.

Cavitation erosion testing was carried out using a modification to ASTM G32-92. This modification is commonly used to test coatings due to the problems presented with coating adhesion to the vibrating tip of the piezoelectric driven horn. A schematic of the erosion experiment is shown in Figure 12. Testing of the samples was carried out by placing the surface of the coating 0.5 mm below the vibrating tip of the horn. The horn tip was replaced prior to each sample tested. The temperature of the water was maintained at 25 °C using cooling coils.

Cavitation erosion experiments were run for a testing interval, usually 100 minutes, followed by drying for 20 minutes in a vacuum oven at 110 °C. This drying step was determined experimentally to be sufficient to remove all water from the coating. After drying, the sample was cooled and weighed. Cumulative mass loss was recorded to determine resistance to cavitation erosion. In addition to mass loss, the surface topography of the coating was examined using a Hommel T8000 surface profilometer (Hommel America, New Britain, CT). Measurement was done using a TK300 contact probe tracing over 23 mm at 0.5 mm s⁻¹ and a cut-off length of 2.5 mm. The profile was measured across the same diameter after each test interval. After measurement the sample was returned to testing. Profile measurement allowed an estimate of the remaining coating thickness.

3. RESULTS AND DISCUSSION

3.1 Starting Powder

The starting powders were examined using XRD, oxygen and chemical analysis, and DSC. This testing was done to look for pre-existing trends in the glass-forming ability of the starting powders at various levels of oxygen contamination, as well as to develop a baseline to which the coating analysis could be compared. The results of the oxygen, DSC, and chemical analysis are presented in Table 4.

Oxygen measurements are given in weight percent while the composition is given in atomic percent on a metals basis. The metals-basis compositions of all starting powders were close to that of the target composition of $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_8\text{Si}_1$. The oxygen levels of the powders ranged from 0.129 to 0.778 wt.% due to differences in atomization. These differences are possibly due to the variation in quality of the atomization gases for each run, or the system in which the atomization was performed.

Table 4. Oxygen content and composition of starting powders.

Sample Label	Metallic Composition (at. %)					Oxygen Content (wt. %)	%Amorphous	$T_g(^{\circ}\text{C})$
	Cu	Ti	Zr	Ni	Si			
Nominal	47	33	11	8	1			
<i>a</i>	46.96	33.40	10.49	8.19	0.97	.1292	99	432
<i>b</i>	46.66	32.77	11.00	8.94	0.63	.2510	73	432
<i>c</i>	46.88	33.48	10.43	8.17	1.04	.3298	71	428
<i>d</i>	46.90	32.47	10.84	9.23	0.57	.3791	67	428
<i>e</i>	47.89	33.78	10.93	6.81	0.59	.7130	52	428

Analysis of the starting powders do not show obvious evidence of crystalline diffraction, as determined by XRD for the two lowest oxygen powders, *a* and *b*, Figure 20. The higher oxygen samples, *c*, *d*, and *e* show peaks associated with crystalline structures. The observed lack of crystalline features in the lower-oxygen powders is supported by the DSC data shown in Figure 14. The thermograms for Powders *a* and *b* show a definite glass transition and large crystallization enthalpies. The amount of amorphous structure present in the starting powders is plotted as a function of oxygen content in Figure 15a. As illustrated

Figure 13. XRD of starting powders. Refer to Table 4 for powder label descriptions.

Figure 14. DSC of starting powders. Refer to Table 4 for powder label descriptions.

3.2 Plasma arc sprayed coatings

3.2.1 Glass formation in plasma arc sprayed coatings

Coatings were deposited for each starting powder under APS and VPS conditions at spray distances of 8, 13, 18, 23, and 28 cm. It was determined during initial screening of the coatings by XRD that the tiles sprayed at 8 cm had all been overheated during spraying. The overheating was not unexpected as the plasma plume was in contact with the substrates during the spray run. This was particularly obvious during VPS spray runs where the lower pressure elongated the plasma. Because of the problems caused by this overheating, which include coating delamination, sample loss due to fixture failure, and deleterious changes in the coating structure it was determined that a spray distance of 8 cm is unsuitably short for this coating system and the tiles produced at this stand-off were excluded from further analysis.

The coatings deposited by PAS show a wide range of changes in oxygen levels with the primary influence appears to be spray environment rather than the starting oxygen levels in the powders. Coatings sprayed by APS exhibited high levels of oxidation (2 - 7 wt.%) accompanied by changes in chemistry while coatings sprayed by VPS show little change in chemical composition with relatively small increases in oxygen content (0.25 - 1 wt%). The oxygen levels of all starting powders and coatings are plotted in Figure 16 for comparison. The measured oxygen values for all powder and coating samples are given in Table 4 and Table 5, respectively.

The oxygen contents of the VPS coatings, while relatively low, were still higher than those of the starting powders. In some cases the oxygen content more than doubled (e.g., Powder *a*). The oxygen levels of the VPS coatings seem to be independent of spray distance, as seen from the nearly constant O levels with increasing stand-off for each powder, Figure 16 for the VPS coatings. This would indicate that oxidation is occurring during the initial melting and is not a function of time of flight.

That is to say, starting powders with higher O levels produced coatings with correspondingly higher O levels for a given stand-off.

As previously stated, the oxygen content of all coatings was measured, while only coatings made from starting Powder *a* and *e* were analyzed for chemical composition. The results of these analyses are listed in Table 5. The spray environment, as mentioned earlier, appears to be critical to maintaining the starting chemistry in the coatings (i.e., metallic composition). Very little change was observed in the VPS coatings from both Powder *a* and *e*, but the APS coatings from these powders show significant loss of Cu and Ni accompanied by a relative enrichment in Ti. The loss of Cu in this alloy system is not unexpected when the vapor pressures of the constituent elements are considered. At 2000 °C the vapor pressure of Cu is an order of magnitude higher than that of Si or Ni, and $\sim 10^5$ times that of Zr.³³ If, however, selective vaporization of Cu was occurring solely due to high vapor pressure, the chemical changes should be more pronounced with increasing spray distance and at the lower pressures of VPS. Since this is not the case it is possible that the formation and selective volatilization of a less stable Cu oxide is involved with these changes. Another observation of the relative decrease in Cu is that coatings that showed the loss of Cu also had a lower amorphous fraction by DSC. The shift in chemical composition could lead to an increase in crystalline content as the glass forming ability of an alloy can strongly depend on composition.

X-ray diffraction of the coatings showed a clear difference in the structure of coatings prepared via APS and VPS and corresponds with the differences in their oxygen levels. The APS coatings, shown in Figure 17a, have much higher O levels and show evidence of crystalline diffraction. It is clear that as O levels increase the amount of diffraction from crystalline phases increases also. The VPS coatings appear to be generally amorphous, as seen in Figure 17b. However, a subtle decrease in the width of the diffuse peak can be seen in the higher oxygen content coating (Powder *e*). This is likely due to initial formation of nanocrystals within the amorphous matrix.

The qualitative observations of the crystalline fraction in the coatings evaluated by the XRD patterns are supported by DSC data; increasing oxygen content within the coatings results in decreasing the fraction of the amorphous phase. DSC thermograms corresponding

amounts of a devitrified phase with increasing oxygen content. As shown in Figure 19 this change is evident when looking at the change in T_x as a function of oxygen content. This depression results in a reduction of the supercooled liquid region, ΔT_x . This behavior has been seen with Zr-Al-Cu-Ni alloys prepared by both melt spinning (rapid quench) and ingot casting (slow cooling).³⁴ It is interesting to note that for coatings with similar O content but differing stand-off distance (i.e., VPS coatings) there is no significant change in the amount of amorphous phase present. This implies that all of the crystalline formation is taking place during or prior to coating deposition and not due to substrate reheating, which was more severe in the VPS case.

Figure 18. DSC thermograms of selected (a) APS and (b) VPS coatings. The O content for the coating (wt. %) is shown for each thermogram.

It is generally thought that oxygen contamination serves to reduce the GFA through the formation of oxides that enhance heterogeneous nucleation during cooling.^{34,35} It is interesting to note that even though the coatings invariably had higher O levels than their starting powders, some of the coatings produced XRD and DSC data that indicate amorphous fraction equal to or higher than those of the starting powders. An example of this is coating

3.2.2 Plasma arc spray coating microstructure

Observations of the polished cross-sections of the coatings display several interesting details. Coating densities are typical of those seen for conventional metallic coatings made from starting powders with similar size fractions, but the pore and splat geometry reflect the higher viscosity of the molten droplets as they impacted upon the surface. This is seen in the both long, flat pores between splat boundaries and larger, spherical pores shown in Figure 21. This viscosity difference is seen in atomized powder of metallic glass alloys, which often contain long ribbons and filaments not usually associated with atomized powders of crystalline metals. This higher viscosity is commonly seen in all supercooled liquids and is, as stated, a mechanism by which nucleation and growth of the crystalline phases is suppressed due to decreased diffusion. Diffusion in similar metallic glass-forming systems has been seen to be ~ 3 orders of magnitude greater than that found for simple metallic systems.³⁶

The measured changes in chemistry reported for the APS coatings above are evident in the micrographs in Figure 21b. The polished cross-sections of APS and VPS coatings using BSE imaging show darker gray regions near splat boundaries of the APS coating. Analysis of these regions using EDS indicates that the dark areas are rich in Ti and Zr, Figure 22. This type of feature in thermal sprayed coatings is often associated with oxide formation on the surface of individual splats due to oxidation during flight. The EDS scan included a check for oxygen location but the results showed only a uniform distribution of oxygen indistinguishable from the background data. This is not surprising, as EDS is not particularly sensitive to O.

In order to more closely examine the dark regions in the APS coating, a sample of the *eAl3* coating was fractured in-situ and observed using SAM. The inter-splat fracture surface shows oxygen enrichment on the surface of an exposed splat as seen in Figure 23. This surface appears to be an outer shell of a splat, which is high in oxygen. The fractured edge of this shell shows a relatively smooth intergranular fracture surface like that commonly seen in crystalline materials, Figure 23a. In contrast, the bulk of the underlying splat has a vein-patterned fracture surface, which is often associated with stress-induced fracture in amorphous materials and is thought to be a result of localized melting.³⁷ The presence of

the coatings displayed features typical of other metallic PAS coatings while illustrating the higher viscosity of the molten glass-forming alloys during deposition. Increasing spray distance for the VPS coatings did not significantly change the O content or amorphous fraction for a given starting powder. However, for the APS coatings, increased stand-off resulted in higher O content and a lower amorphous fraction in the coating. Additionally, the crystalline phases that are seen appear to be forming due to the spraying and deposition of the coating rather than due to substrate reheating by subsequent coating passes.

Results obtained from all coatings via XRD and O measurements indicated that coatings made from starting Powders *b*, *c*, and *d* should exhibit coating characteristics intermediate to that measured for the extremes of oxygen content (i.e., Powder *a* and *e*) and thus were excluded from DSC and chemical composition measurements. Coatings were chosen for cavitation erosion testing based on examining the extremes among coatings to determine if any observable effects of the oxygen contamination or associated amorphous fraction could be seen as a result of cavitation erosive wear.

Figure 22. EDS data from coating *aAl3* showing (a) BSE image at 1000x, (b) Zr concentration, (c) Cu concentration, and (d) Ti concentration.

of the statistical variation of the microstructural features typically seen in thermally sprayed coatings. Each coating contains a network of splats, splat boundaries, oxide particulates, crystalline phases, amorphous phases, and micro-cracks. It is expected that these features respond differently to the stresses induced by cavitation erosion, as shown in Figure 25.

Though no quantitative conclusion can be drawn from the mass-loss data, visual inspection of the coatings shows that samples from the same coating groups tend to exhibit damage in a similar manner. Examples of the damage are shown in Figure 26. The 3-fold cracking in Figure 26b is observed in VPS coatings of *eV13* and is seen in all tested samples of that group. Likewise, networks of deep cracks developed early in the cavitation erosion experiment, typically ~100-200 minutes for coatings of *eA13*. The previously mentioned cracking was not taken to be failure of the coatings until a fault appeared, through which the substrate could be visually observed. Failure is clearly evident in sample *eA23* shown in Figure 26b.

Figure 25. Polished cross-section of a cavitation erosion wear scar illustrating fracture along splat boundaries in both (a) VPS and (b) APS coatings.

4. CONCLUSIONS

This research has shown that it is possible to deposit coatings of gas atomized $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_8\text{Si}_1$ powders containing various levels of oxygen contamination using plasma arc spray methods. The structure of the coating was found to depend primarily on the spray environment, with an argon atmosphere producing the most amorphous samples for a given starting powder. The oxygen content of the coatings reflected the relative levels of the oxygen contamination in the starting powders.

The analysis of the starting powders displayed oxygen contents ranging from 0.125-0.79 wt.%. It was shown that higher oxygen levels lead to more crystalline structure in the starting powders as determined by XRD and DSC. This trend was found to be true for both the starting powders and for the plasma sprayed coatings. Chemical composition for all starting powders was very close to the nominal alloy composition. Chemical changes in the coatings involved the loss of Cu in coatings where high levels of oxidation were found.

Cavitation erosion testing of selected coatings showed a weak trend that coatings prepared by VPS had lower damage rates, but there was no clear data to indicate which coating parameters were superior. The range of data produced from testing duplicate coating was too wide to provide a good statistical measure of cavitation erosion resistance. Of interest was the fact that when coatings began to show damage from cracking, all samples of a group showed similar damage and usually the damage pattern was somewhat unique to that group of samples. Failure of the coatings was due to features inherent to PAS coating (i.e., pores, splat boundaries, oxide inclusions) rather than the mechanical characteristics of the amorphous alloy.

This research produced no specific reason for the effect that oxygen has on the glass formation in PAS coatings prepared with this alloy. There are, however, many papers that have looked at this question for other systems. Further investigation, especially utilizing transmission electron microscopy and Auger microscopy might give a better indication of where the oxygen is found in the coatings and what effect it has on the mechanical characteristics. Oxides are potent heterogeneous nucleation sites that have been shown to

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